Atomic Energy Control Board
P.O. Box 1046
Ottawa, Canada
K1P 5S9

Commission de contrôle de l'énergie atomique
C.P. 1046
Ottawa, Canada
K1P 5S9

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REMEASUREMENT OF TH-230 IN THE POREWATER OF LACNOR TAILINGS

by

W.J. Snodgrass
and
D.R. Hart
Beak Consultants Ltd.

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REMEASUREMENT OF THORIUM-230 IN THE PORE WATER OF LACNOR TAILINGS

A report presented to the Atomic Energy Control Board by W.J. Snodgrass and D.R. Hart, Beak Consultants Limited.

ABSTRACT

A resampling of the Lacnor tailings management area was undertaken under a comprehensive quality assurance programme to establish levels of thorium 230 in pore water. A quality assurance programme was established for field sampling, sample handling and transport, and laboratory procedures and reporting. The external audit was used to evaluate analytical bias (on synthetic and field samples) and precision (by comparison of duplicate-duplicate results). Accuracy was assessed using synthetic samples. The external audit indicates that thorium 230 measurements by the main laboratory are not significantly different from the interlaboratory average within standard statistical limits. The results of the audit are based on measurements of environmental samples and known synthetic samples. This shows that present and previous measurements of thorium 230 varying from 0,1 to 150 Bq/L are valid data.

A qualitative interpretation of the controls on thorium 230 geochemistry is provided in terms of control by thorium 232 and thorium dioxide(c) solid phase. Generic dose estimates for consumption of water containing thorium 230 are made but require refinement to account for the actual pH of the drinking water and the degree of dilution of the pore water.

The results of this project indicate that the performance of the laboratory that will conduct future thorium 230 measurements can be assessed satisfactorily with a smaller scale external laboratory assurance programme. The programme should include replicate samples sent to each laboratory and interlaboratory comparison on samples having high and low values of thorium 230.

RÉSUMÉ

On a prélevé de nouveaux échantillons de l'aire de stockage des résidus de Lacnor dans le cadre d'un programme global d'assurance-qualité pour établir la teneur en thorium 230 dans les eaux interstitielles. Un programme d'assurance-qualité a d'abord été établi pour l'échantillonnage sur place, la manipulation et le transport des échantillons, les analyses en laboratoire et la présentation des rapports. On s'est servi de vérifications externes pour évaluer d'abord le biais analytique des échantillons synthétiques et pris sur place, puis la précision par comparaison des doubles de résultats. L'exactitude a été estimée à partir d'échantillons synthétiques. Selon la vérification externe, les mesures de thorium 230 du laboratoire principal ne sont pas très différentes de la moyenne atteinte entre les laboratoires à l'intérieur de limites statistiques normales. Les résultats de la vérification sont basés sur les relevés d'échantillons environnementaux et d'échantillons synthétiques connus. Ceci montre que les relevés actuels et antérieurs de thorium 230 variant de 0,1 à 150 Bq/L sont valides.

Une interprétation qualitative des contrôles des caractéristiques géochimiques du thorium 230 est fournie en termes de contrôle du thorium 232 et du bioxyde de thorium (c) en phase solide. Des estimations générales des doses dues à la consommation d'eau contenant du thorium 230 sont avancées, mais demandent à être raffinées pour tenir compte du pH réel de l'eau potable et du degré de dilution des eaux interstitielles.

Les résultats du présent projet indiquent que la qualité des mesures des laboratoires qui effectueront les relevés futurs de thorium 230 peut être évalué de façon satisfaisante en utilisant le programme d'assurance-qualité d'un petit laboratoire externe. Ce programme devrait inclure des échantillons en double à envoyer à chaque laboratoire pour pouvoir comparer les résultats des échantillons à forte et faible teneur en thorium 230.

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1.0 INTRODUCTION AND STUDY OBJECTIVES

1.1 Significance of Thorium-230 in Environmental Management

Th-230 levels in the pore water of uranium mill tailings and receiving waters have the potential to cause a dose to human beings which may be of concern. Th-230 measurements made recently (Golders et al., 1986) in the Lacnor tailings have been shown to be higher than previously thought probable. These measurements have been made upon acidic tailings where the solubility limit of Th-232 permits elevated concentrations. Activity levels for these two radionuclides of the order of 10 Bq/L and higher have been observed. Such levels are of potential concern to regulatory authorities who evaluate doses to humans.

Relatively precise estimates of Th-230 and its sister radionuclide, Th-232, are required in order to determine the geochemistry of Th-230 and to predict the long-term concentrations of Th-230 in the tailings. The long-term is of concern to agencies, such as the AECB, because future geochemical changes have the potential to increase the concentrations of Th-230 in pore water by an order of magnitude or more. Such levels could cause an associated increase in activity in receiving waters.

1.2 Study Background

Th-230 activity has been previously measured in the acidic Lac Nor tailings management area (Golders et al., 1986), in both the pore water and the surface water. Samples were collected from seven boreholes (Figure 1.1), labelled: GW-01, GW-02, GW-04, GW-05, GW-06, GW-07 and GW-08, and analyzed for a variety of cations, anions and radionuclides (U, Ra-226, Th-228, Th-230, Th-232, Ra-228, Pb-210 and Po-210). The analytical results from the previous study and the field procedures from the Golders et al. (1986) study are given in Appendix A.

The analytical measurements were made under a quality assurance program which involved submission of a duplicate sample to a check laboratory for every 10 to 15 samples. The quality assurance results are given in Appendix A.1 as "Table 1.10 and 1.11" from Golders et al. (1986). A few of the results are abstracted from the appendix and summarized on Table 1.1. The analytical results from the "check" laboratory are indicated by Golders et al. (1986) using the terminology "DUPLICATE" in the third

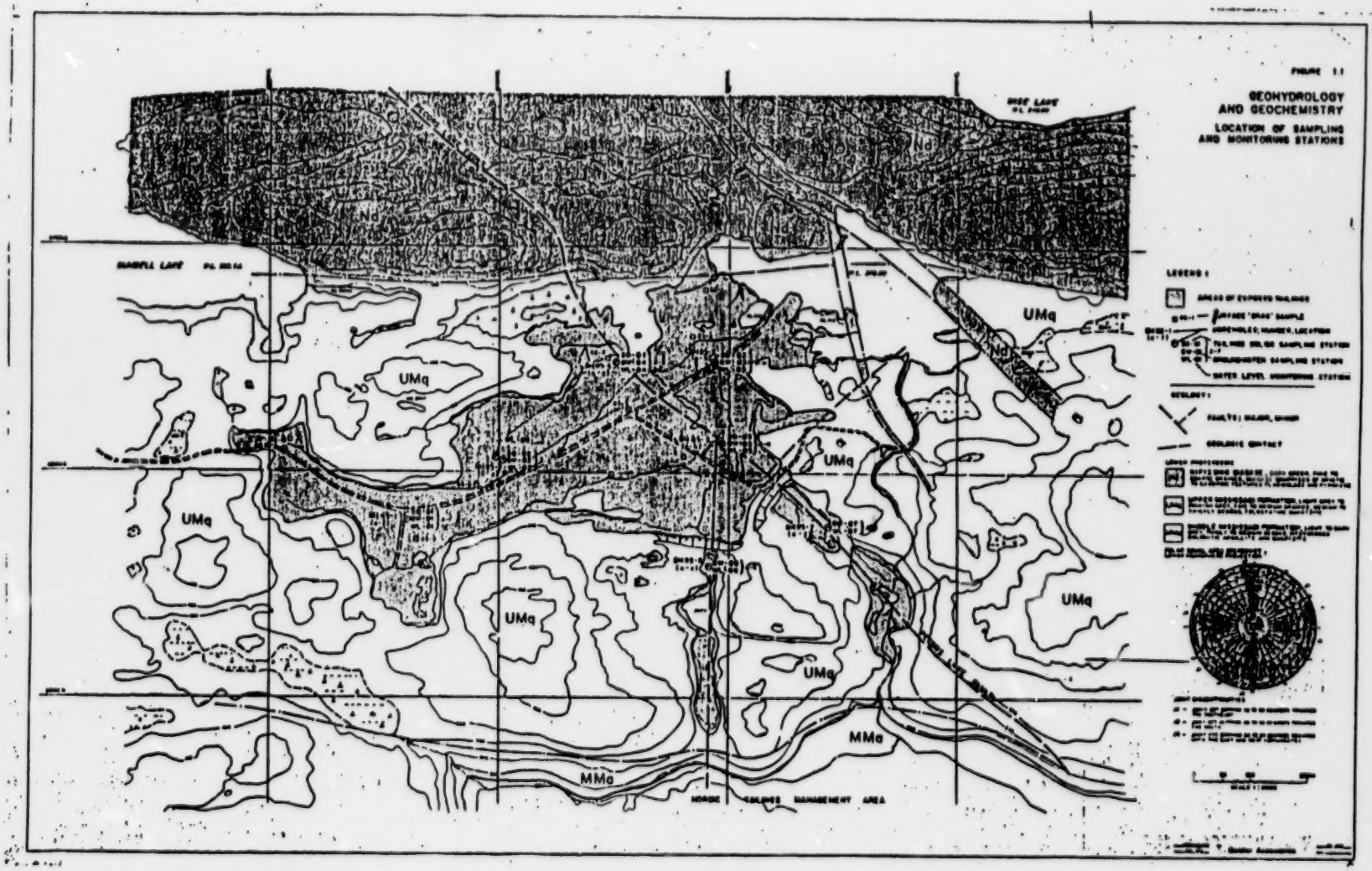


FIGURE 1.1: LOCATION OF PIEZOMETERS AND SURFACE WATER SAMPLING SITES (after Golders et al., 1986)

TABLE 1.1: SUMMARY OF A FEW OF THE QUALITY ASSURANCE RESULTS FROM GOLDERS ET AL. (1986) STUDY

Site	Piezo-meter	Tip Material	Depth (m)	Temp (°C)	DO (ppm)	pH	U (ppb)	Ra-226 (Bq/L)	Th-228 (Bq/L)	Th-230 (Bq/L)	Th-232 (Bq/L)
GW-01	b	R	11.84	7.0	0.80	4.9	5.9	1.65	0.08	1.84	0.08
GW-01	b	Duplicate					5.0	.39 ±.04	LT .005	.036 ±.012	.006
GW-02	I	T	7.90	8.0	0.95	5.0	9,800	15.00	0.66	13.00	0.66
GW-02	I	Duplicate					13,000	2.28 ±.13	N/A	1.68 ±.07	N/A
GW-05	a	ST	18.34	6.8	0.50	5.1	17.0	1.54	0.02	1.61	0.02
GW-05	a	Duplicate					19.5	.31 ±.04	N/A	.021 ±0.111	N/A
GW-07	t	R	8.14	5.2	0.60	7.2	3.7	0.04	0.05	0.10	0.05
GW-07	t	Duplicate					LT .5	.022 ±.011	LT .005	LT .005	LT .005
GW-03	f	T	4.62	6.5	0.45	6.05	110	4.76	0.03	1.00	0.03
GW-03	f	Duplicate					170	6.9 ±.3	.06 ±.01	.02 ±.01	LT .01
GW-05	e	T	9.24	7.0	0.6	5.95	60	4.55	0.09	1.32	0.09
GW-05	e	Duplicate					170	3 ±.2	.14 ±.01	.05 ±.01	LT .01

column of Tables 1.10 and 1.11; this column was labelled "Tip Material". The results of the quality assurance program indicated that there was an order of magnitude or more variation in Th-230 measurements between the two laboratories. The accuracy of the results cannot be assessed because a "known" sample was not submitted. A consensus value for environmental samples cannot be determined due to the use of one check laboratory.

These results were unsatisfactory. The quality of data describing the level of Th-230 activity in these tailings was uncertain because the differences between laboratories are too large, and only two laboratories were involved. Accordingly, the appropriate values for Th-230 levels in groundwater and surface water for dose commitment calculations, and the geochemistry of Th-230 in the pore water of tailings cannot be characterized with assurance.

In the previous sampling work on Lacnor, the "best hypothesis" suggested that the "sample preservation technique" rather than "analytical differences between laboratories" was the cause of the order of magnitude discrepancy between Th concentrations. The waters sampled are highly acidic (pH 2 to 3), and contain high concentrations of Fe(II). Despite use of acid preservation (to pH 1.5), iron hydroxide precipitates were observed in the bottom of a few sample bottles. It is the hypothesis of Golders et al. (1986), that some of the laboratories did not analyze these precipitates (if any) for Th-230.

There are available complexing agents which stabilize Fe(II) (i.e., prevent its oxidation, e.g., ascorbic acid) and which complex thorium to maintain it in solution. We have considered such agents for preservation of these samples. Due to potential interferences of this complexing agent and conversations with CANMET scientists, it was decided that acidification to pH 1 would be the most appropriate preservation technique.

1.3 Study Objective

The objective of this study was:

- to resample the same piezometers installed for the Lac Nor field program and to remeasure Th-230 within the framework of a comprehensive quality assurance (QA) program.

1.4 Future Use of Data

The results of this study will provide reliable information on the environmental behaviour of Th-230 in such sites. It can be used by the AECB and other agencies as background for assessing Th-230 in derived release limit calculations and in decommissioning submissions made by uranium mine and mill operators. A qualitative interpretation of the geochemistry of Th-230 in the tailings pore water is provided in this report to aid interpretation of the levels obtained.

2.0 SAMPLING PROGRAM DESIGN AND QUALITY ASSURANCE PROGRAM

2.1 Field Sampling Procedures

A specific set of procedures were established in the office prior to sampling to assure a high level of quality and consistency during the field sampling phase of the project. Based upon the previous measurements made by Golders et al. (1986), a field form was designed to record pertinent field information and sample bottle numbers for each piezometer. A blank field form is given in Appendix A.3. As well, an initial selection of 30 (of the 45) piezometers installed by Golders for sampling was made in the office prior to departure.

Field personnel drove a van carrying all necessary equipment and empty sample bottles from Toronto to Elliot Lake. All sample bottles were new; they were soaked in acid to remove any residual contaminants and rinsed with distilled water prior to transport to Elliot Lake. The senior field technician is a hydrogeologist with three years experience in installation and sampling piezometers. The field personnel were thoroughly briefed on what to expect at the site and program requirements related to sampling and sample handling prior to departure.

The same set of safety procedures as used previously by Golders personnel (Golders et al., 1986) were followed. These included procedures for handling acids, radiation monitoring badges, a two-man crew, and contacting Rio Algom security concerning when they were on the tailings site.

An initial reconnaissance was made of the Lac Nor site on Tuesday, 30 October 1987. The weather was foggy and close to freezing in the morning; in the mid-afternoon, the weather changed to cold, windy and sleet/snow. The weather continued this way for the remainder of the sampling periods through 2 November 1987. An initial inspection to ascertain the condition of each piezometer indicated that they were all undamaged, capped and distinctly identified (scratched or black marker numbering on the PVC pipe). The length of piezometer pipe above the ground surface was recorded during the initial inspection.

New 5/8 inch and 1/2 inch polyethylene tubing was installed in each piezometer prior to flushing the piezometers and collecting samples. Previous tubing found in the pipe was discarded except in piezometer nest GW01. In this nest, the sampling tube was of a similar size (0.5 inch diameter) to the new tubing, the tubing was in good condition with its end folded and the piezometer capped. Hence, it was retained for use. All piezometers were in good shape with their ends properly capped. Various lengths of tubing were needed, depending upon the depth of the piezometer; an extra 0.75 to 1.0 metres of tubing was left at the top of the piezometers to facilitate sampling. The extra tubing was folded and pushed into the piezometer after each flushing/sampling interval.

After removal of the old tubing and prior to tubing installation, the depth to water in each piezometer was recorded using a Solinist water level tape. The probe tip was wiped with paper towels between each measurement. If more than the tip was submerged below the water level, the submerged portion was rinsed with distilled water.

Flushing and sampling of the piezometers was performed with a Waterra hand pump system. This system is composed of a Delrin foot valve attached to the dedicated tubing. The foot valve has a ball valve on the bottom that permits water intake into the valve during downward motion of the tube and closes during the upward motion. Water is pumped to the surface by generating upward momentum in the column of water flowing up through an oscillating discharge tube. This pumping system is fast, simple and minimizes the potential for cross contamination between wells because the foot valve is the only inter-changeable part.

Foot valves were attached before each flushing/pumping, and then removed at the completion of the flushing/pumping activity. To install the foot valve, the tubing had to be withdrawn from the wells; after withdrawal, it was coiled above the piezometer to prevent it from touching the ground surface. The foot valve was then attached to the tubing and the combined foot valve/tubing reinserted into the well. Removal of the foot valve was similarly done. After removal from the tubing, each valve was washed in nitric acid and rinsed with distilled water to minimize the potential for cross contamination. Each footvalve was consecutively washed with different solutions of 1:3 nitric acid and 1:5 nitric acid; they were next rinsed with distilled water and then inserted in 2 distilled water baths. They were then wrapped in paper towels. To avoid the effects of sleet/snow, the washing procedures were carried out in the protection of the van.

All piezometers had the new tubing installed and flushing completed on the same day. Piezometers were flushed to remove all the standing water in the tubing. For wells that responded quickly, three pore volumes were removed. Slowly responding wells were pumped dry. During the flushing period the characteristics of the water (colour, turbidity, odour), the final pumping depth, and the volume of water removed were recorded.

During the process of replacement of old tubing, flushing and sampling, procedures being used by field personnel were evaluated by a third professional who flew in from Toronto. This evaluation showed that procedures stipulated in the office by the senior contaminant hydrogeologist were being followed, but that a small change in procedure would be useful involving an extra acid wash (1:5 nitric acid) prior to the distilled water rinse.

Groundwater sampling was performed on two consecutive days following flushing. All groundwater samples were filtered through a disposable 0.45 micron filter membrane. The volume of water that was filtered by one filter membrane was dependent on the turbidity of the sample and usually ranged between 2 and 4 litres. New filters were used on each piezometer. If a second sample was taken from a piezometer after it had recharged, a new filter membrane was used. Sample containers were appropriately numbered and recorded just prior to sample collection. Samples for anion analysis were collected in either a 400 mL or 1 litre wide mouth plastic jars. Samples to be analysed for radionuclides and metals were collected in 1 or 4 litre plastic jugs. Radionuclide and metal samples were further preserved with 40 mL of nitric acid per litre of sample to pH less than one. The pH was checked after preservation in a few samples. The volume of water removed from each well was recorded; the volume was dependent upon the ability of the piezometer to recharge and on whether duplicate analysis were to be performed. For most samples, a minimum of 1.5 litres of groundwater was collected. In some cases, specific wells with sufficient recharge had to be substituted for piezometers initially targetted for QA purposes due to insufficient sample volume being obtained from these piezometers.

Field measurements of temperature, pH and specific conductance were made upon filtered samples, placed into 400 mL plastic jars. Results were recorded on the field sheets. The instrument probes were rinsed with distilled water before and after measurements. The pH and specific conductance meters were calibrated in the office

prior to the commencement of field work. Their calibration was checked in the field before sampling began on each day and after every five to six measurements.

During sample collection, samples were kept cool in the BEAK van which maintained an average temperature of 0 to 4°C due to the cold daytime temperatures. At the end of the sampling day, the samples were stored in a cool room until being reloaded onto the van for transportation back to Toronto. Also, at the conclusion of each day, all field sheets were inspected to make sure that they were in order, and a telephone call made to Toronto to discuss selection of wells for duplicate chemical analysis and to discuss any sampling problems encountered.

Field blanks were obtained by pumping distilled water through a dedicated in-line filter into a sample bottle. Surface water samples were collected at SW-01 and SW-02 by collecting water overflowing the weirs directly into the sample bottles. Field parameters (e.g., pH) were measured similarly to procedures used for pore water sampling.

After return to Toronto, field notes were collected and filed and used for sample submittal. A summary of field abbreviations on the conditions of each piezometer, etc. was prepared and is given in Table 2.1. A debriefing meeting with senior project staff was held and any deviations from field sampling procedures initially developed, discussed. There were no major deviations.

2.2 Sample Handling and Shipment

The main objective of this component of the study was to ascertain that the samples did not lose their validity due to improper handling, labelling or accidents during transport. All samples were taken and placed in the BEAK van and then stored temporarily in a building overnight to avoid freezing. They were then transported in the same van back to Toronto. Accordingly, the major quality assurance activity of this study component was sample labelling.

The field sample form was used as the chain of custody for tracing sample bottles from the time of field sampling to the time of submittal to the radionuclide laboratories. Upon return to Toronto, all sample bottles were laid out on the floor and grouped

TABLE 2.1: OBSERVATIONS FOR PIEZOMETERS AT THE LACNOR TAILINGS SITE

				FLUSHING					SAMPLING					
Piezometer	Static Water Level (mbct)	Water Level Depth Below Surface (m)	Approx. Borehole Volume (L)	Time	Total Volume Removed (L)	Charact. of Water colour/turbidity/odour	Final Depth to Water After Pumping (mbct)	Comments	Date/Time	Depth to Water (mbct) Before Sampling	Depth to Water (mbct) After Sampling	Volume Removed (L) Anion	Volume Removed (L) Metals/Radio.	# of Filters Used
GW01-a	1.84	0.73	3.0	8:30	3	yellowish, med., none	8.17 - dry		87/11/05 - 16:00	1.77	8.01	0.4	1.5	1
GW01-b	2.01	0.76	7.5	8:50	15	yellow-brown, med., sulphur	3.20		87/11/06 - 8:00	2.60	3.09	1	8	2
GW01-c	1.63	0.71	NA*	9:15	3	grey, high, sulphur	6.80 - dry	flushed twice	87/11/06 - 8:00	1.73	4.25	0.4	2	1	pumped 1.5 L/let stand for 10 min., pumped again
GW01-d	0.96	0.73	NA	9:15	3	grey, high, sulphur	4.00 - dry	flushed twice	87/11/06 - 9:00	0.80	-	0.4	2	1	
GW01-e	0.14	-0.27**	1.8	9:30	0.8	grey, med., organic	2.56 - dry		87/11/06 - 9:00	1.01	-	0.1	0.9	1	pumped on 3 separate occasions
GW01-f	0.94	0.70	NA	9:40	1	grey, med., organic	1.31 - dry	flushed twice	-	-	-	-	-	-	not sampled - low volumes
GW02-a	0.30	-0.29	11.7	10:25	36	grey, med., organic	2.56		87/11/05 - 8:00	1.27	1.32	0.4	4	1	
GW02-b	0.23	-0.21	10.3	10:45	15	grey, low, organic	12.0 - dry		87/11/05 - 8:00	1.63	8.00	1	9	2	difficult filtering
GW02-c	0.36	-0.37	7.6	11:00	3.5	yellow, low, organic	dry		87/11/05 - 9:00	2.10	6.22	0.4	4	1	
GW02-d	1.01	0.57	1.5	11:00	1	grey, low, organic	2.10 - dry		87/11/05 - 10:00	1.0	-	0.4	0.3	1	could not get volume on 3 occasions
GW02-e	1.06	0.59	0.3	11:10	0.3	grey, low, organic	1.60 - dry		-	1.22	-	-	-	-	not sampled - low volumes
GW03-i	1.63	0.44	6.7	11:25	21	clear, low, organic	3.06		87/11/05 - 11:00	1.68	3.05	0.4	4	1	
GW03-ii	1.35	0.44		11:40	10	yellow, low, organic	3.83 - dry		87/11/05 - 12:00	1.35	3.70	0.4	3.3	1	difficult filtering
GW03-iii	1.63	0.47	3.3	11:55	7	yellow/grey, low, organic	5.78 - dry		87/11/05 - 12:00	1.76	4.00	0.4	4	1	
GW03-iv	1.02	0.43	4.4	11:50	5	yellow/grey, low, organic	4.78 - dry		87/11/05 - 13:00	1.26	2.60	0.4	3.75	1	
GW03-v	1.82	0.42	3.6	12:10	3	clear, low, organic	4.26 - dry		87/11/05 - 13:00	2.02	3.00	0.4	9	2	
GW03-vi	1.83	0.42	2.7	12:10	2.5	yellow/grey,low, sulphur	4.32 - dry		87/11/05 - 13:00	0.92	3.05	0.4	2	1	difficult filtering
GW03-vii	1.08	0.40	1.9	12:25	2.5	grey, low, sulphur	2.30 - dry		87/11/05 - 14:00	0.96	-	0.4	6	2	pumped 3 separate occasions
GW03-viii	1.83	0.49	0.8	12:15	1	grey, low, organic	NR - dry		-	-	-	-	-	-	not sampled - low volume
GW03-a	0.38	-0.17	8.7	14:30	8	grey, med., sulphur	8.53 - dry		-	-	-	-	-	-	not sampled
GW03-b	0.64	-0.06	7.5	14:40	6	grey, med., sulphur	10.00 - dry		87/11/06 - 13:00	0.84	-	0.4	2	1	
GW03-c	0.78	0.02	6.3	13:05	6	grey, med., organic	9.57 - dry		87/11/06 - 13:00	0.54	-	1	4.5	2	sampled on 2 occasions
GW03-d	0.44	-0.08	5.6	13:00	3	grey, medl, organic	8.22 - dry		-	-	-	-	-	-	not sampled
GW03-e	0.54	-0.02	4.3	13:15	3	grey, med., organic	6.22 - dry		87/11/06 - 14:00	0.54	-	0.4	1.5	1	
GW03-f	0.55	0.04	3.2	13:25	2.5	grey, low, organic	5.76 - dry		87/11/06 - 14:00	0.34	-	0.4	1.5	1	
GW03-g	0.69	0.07	2.1	13:25	1.5	grey, med., organic	3.78 - dry		87/11/06 - 14:00	0.63	-	0.1	1	1	
GW03-h	1.19	0.05	0.8	13:30	0.6	yellow, med., organic	2.08 - dry		-	-	-	-	-	-	not sampled - low volumes
GW04-a	1.26	0.11	8.1	13:15	7	grey, low, organic	11.82 - dry		87/11/06 - 15:00	1.20	7.0	0.4	2.0	1	
GW04-b	0.73	0.24	6.0	13:15	4	grey, low, sulphur	9.00 - dry		87/11/06 - 15:00	0.73	8.0	0.4	2.0	1	
GW04-c	0.73	0.23	4.8	13:30	3.5	grey, low, organic	7.46 - dry		87/11/06 - 15:00	0.67	5.39	0.4	2.0	1	
GW04-d	0.93	0.27	4.0	13:55	2.5	grey, low, organic	6.79 - dry		87/11/06 - 16:00	0.93	-	-	-	-	not sampled
GW04-e	0.81	0.14	2.6	13:30	2.5	grey, low, organic	4.43 - dry		-	-	-	-	-	-	not sampled
GW04-f	0.68	0.26	1.8	14:00	1	grey, med., organic	3.02 - dry		-	-	-	-	-	-	not sampled
GW04-g	0.63	0.70	NA	14:05	1	grey, med., organic	1.67 - dry		-	-	-	-	-	-	
GW05-a	3.73	3.03	10.7	15:55	8	grey, med., organic	13.0 - dry		87/11/06 - 11:00	3.66	-	0.4	2.0	1	
GW05-b	3.05	2.43	12.3	16:15	17	grey, med., sulphur	27.3 - dry		-	-	-	-	-	-	not sampled
GW05-c	3.76	2.86	13.3	16:30	10	grey, low, organic	19.1 - dry		87/11/06 - 11:00	3.66	9.12	0.4	6	3	2 separate sampling periods
GW05-d	1.30	0.71	6.9	16:55	3	grey, med., organic	9.7 - dry		87/11/06 - 11:00	1.48	7.55	0.4	2	1	
GW05-e	1.61	0.35	6.0	17:05	3.5	red-grey, med., sulphur	10.48 - dry		-	-	-	-	-	-	not sampled
GW05-f	1.10	0.32	5.0	16:05	3.5	grey, med., organic	6.2 - dry		87/11/06 - 12:00	1.15	7.02	0.4	2	1	
GW05-h	1.26	0.41	3.8	16:00	3.5	grey, low, organic	6.50 - dry		87/11/06 - 12:00	1.35	-	0.4	1	1	pumped dry
GW05-i	0.73	0.29	2.8	NR	2.5	NR	4.10 - dry		-	-	-	-	-	-	not sampled
GW05-j	0.59	0.11	1.9	NR	1.5	NR	3.40 - dry		-	-	-	-	-	-	not sampled
GW05-k	0.63	0.03	0.7	NR	0.7	grey, low, organic	1.62 - dry		-	-	-	-	-	-	not sampled
SW01	-	-	-	-	-	-	-		87/11/05 - 15:00	-	-	1	3	-	reddish colour to water
									87/11/06 - 17:00	-	-	0.4	4	-	
SW02	-	-	-	-	-	-	-	-	87/11/05 - 15:00	-	-	0.4	8	-	reddish colour to water
									87/11/06 - 17:00	-	-	0.4	4	-	

* NA - depth not available
** indicates water level is above the ground surface
NR observations not recorded

according to piezometer nest and type of sample, and checked against the field sample forms. All were accounted for. Anion samples were stored in a 4°C cold room until shipment to the relevant laboratory. Radionuclide samples preserved with nitric acid were stored in a cool (10 to 12°C) room until sample shipment. All radionuclide sample bottles were inspected to see if any ferric hydroxide (brownish) precipitates had formed; in a few samples where this was observed, additional nitric acid was added to bring them back into solution. This was done because of the hypothesis for the discrepancies for Th-230 analyses made previously by Golders et al. (1986).

For sample submittal, a letter detailing analyses requested and the samples were shipped to each radionuclide laboratory by ground courier. Telephone contact was made with each laboratory after transport if any discrepancies were noted by the laboratory between the letter of submittal and the sample description. The major "apparent" discrepancy was that noted by the prime laboratory that several of the 4-L sample bottles were only partially full. They were reassured that this was the proper volume as this was the total sample sampled, or a portion had been taken for submittal to a check laboratory. Generally, the 4-L sample bottle into which the original field sample had been pumped was submitted directly to the main analytical laboratory to minimize sources of contamination. In the case of the check laboratories, new 1-L acid soaked/washed bottles were used to take an aliquot of sample from the 4-L bottle.

2.3 Laboratory Methods and Procedures

2.3.1 Chemical Methods of Analysis

Monenco Analytical Laboratories (MON) Calgary, Alberta, was the prime laboratory for radionuclide analysis. Becquerel Laboratories (BEC) of Mississauga, Ontario, and the Saskatchewan Research Council (SRC) of Saskatoon, Saskatchewan, were used as check laboratories for radiochemical analyses. Radiochemical methods of analysis used by Monenco and SRC for thorium isotopes are detailed in Volume 5, Chemical Methods of Analysis of the Lacnor data report (Golders et al., 1986). Radiochemical methods of analyses used by Becquerel are detailed in BEAK (1987).

Barringer Inc. was the prime analytical laboratory used for cations (including thorium) and anions. Methods, which consisted of ICP for cations and ion chromatography for anions, are also detailed in Golders et al. (1986).

2.3.2 Laboratory Procedures and Quality Assurance Program

Laboratory Procedures

The laboratories used in the analysis were forewarned of the program objectives in order to assure timely attention to the samples and appropriate sample handling. The following types of QA procedures were used by the laboratories:

1. An inspection and sample identification program was made to ascertain that all samples were received at the laboratory and were in good condition on arrival. Chain of custody documentation was in place to permit future tracing of sample history.
2. The laboratories use control chart procedures for controlling the analysis in the laboratory, and use standard methods for doing analysis.
3. The laboratories use daily calibration procedures for these instruments and use internal standards on every 10-15 samples.

Quality Assurance Program

A quality assurance program for auditing the performance of the laboratories was developed and based, in part, upon statistical principles.

It included the following sample submission and check procedures:

1. Submit one-half of the field samples for analysis. After obtaining satisfactory results from the first set of field samples, submit the last set of samples for analysis. This approach was adopted because all samples were obtained on a campaign basis (i.e., a single-event sampling effort), but we did not wish to submit all samples for analysis, receive the results and see that there were discrepancies.

2. Duplicate approximately 20% of the samples, sending each sample to two check laboratories for quality assurance rather than to one.
3. Send replicate samples of each duplicate sample to each laboratory to assess their ability to obtain reproducible values.
4. Submit prepared samples containing known concentrations of Th-230 to each laboratory at the time of sample submittal in a chemical matrix ($FeSO_4/H_2SO_4$) and pH similar to that of the natural water samples.
5. Measure Th-232 by radiochemical techniques so that total thorium calculated from the specific activity of Th-232, and total thorium measured by ICP could be compared as a further QA check. This also permitted examination of the Th-230:Th-232 relationship for outlier samples.

2.3.3 Principles of Quality Assurance Program

The principles of the quality assurance program are outlined below. The basic approach is to use a laboratory round-robin to define the consensus value of environmental samples and to search for an outlier laboratory, if any. To conduct such an approach, a minimum of three laboratories are required to obtain any statistical significance in the data. Five to six laboratories are required to define an outlier laboratories when the data are somewhat variable, as is true of environmental samples. Since only three radionuclide laboratories were available, the robustness of the analysis given in Section 3.4 is limited.

Laboratory performance was evaluated in terms of agreement between laboratories, accuracy of each laboratory relative to target values of synthetic samples and precision within each laboratory. Thus, if there is disagreement between laboratories, it is possible to determine which laboratories are correct, and to estimate the bias associated with the other laboratories.

Audit samples (both replicates and synthetic samples) spanned the concentration range. Piezometers likely to yield high and low concentration samples were known from the previous study and were hence used in the QA program. Audit samples were identified as such to the laboratories.

Split sample Replicates

The split sample audit design was as follows:

Split Sample	Laboratory 1	2	3
1 (low conc.) Replicate 1	=	=	=
3 (high conc.) Replicate 1	=	=	=
3 (low conc.) Replicate 2	=	=	=
4 (high conc.) Replicate 2	=	=	=

Youden's (1969) paired sample technique was used to identify any laboratory that was not in statistical agreement with the others. The technique involves plotting each laboratory in paired sample space, according to its mean determination for each sample. This was done for each pair of samples. The among-laboratory standard deviation for each sample is used to define a 2 standard deviation (SD) elipse, within which all laboratories should fall if they are in agreement. Outlier laboratories can be in one of four quadrants. Quadrants II (top RH quadrant) and IV (bottom LH quadrant) indicate high or low relative bias. Quadrants I (top LH quadrant) and III (bottom RH quadrant) indicate erratic performance (high on one sample, low on the other).

Since the split samples do not have known concentrations, only relative bias can be inferred. If there is disagreement among laboratories, it is possible that the outlier laboratory may be correct.

To address the question of accuracy, a similar analysis was performed on the synthetic samples of known concentration.

Youden plots do not address the question of within-laboratory precision, except insofar as erratic performance and imprecision are often coincident. **Duplicate-duplicate plots were used to evaluate within lab precision.** Each laboratory received a split sample in duplicate. This allows evaluation of a within-laboratory precision. A plot of the high duplicate vs. the low duplicate concentration permits an estimate of precision for each

laboratory. It also reveals any systematic change in precision as a function of chemical concentration. Perfect precision gives a plot intercept of a=ϕ and a slope of b=1. Linear regression analysis will be used to test these hypotheses. If b=1 the within-lab standard deviation is:

$$SD = \frac{a^2}{2}$$

If b is greater than 1, then: $SD_x = \frac{(y-x)^2}{2}$

where: $y = a+bx$, and
x = the low duplicate concentration.

Any consistent relative bias between laboratories, or dependence of relative bias on chemical concentration, is also evident from the duplicate-duplicate plot.

Synthetic Samples

The synthetic sample audit design used was the following:

Split Sample	Laboratory 1	2	3
1 (low conc.)	-	-	-
2 (high conc.)	-	-	-

As previously described for split samples, Youdin's (1969) paired sample techniques was used to identify any laboratory that is not in statistical agreement with the others. However, since the true concentration in this case is known, an acceptance ellipse centred on the design concentration, plus or minus 2 standard deviations can also be constructed. In this study, the interlaboratory mean was essentially the same as the design concentration. Any laboratory falling outside this ellipse on the Youden plot was considered to exhibit an absolute bias (quadrants II or IV) or erratic performance (quadrants I or III).

Isotope Ratios

Consistent relationships were expected between certain thorium isotopes (Th-230, Th-232). Every sample analyzed was checked for adherence to these relationships. Two relationships were examined:

- log (Th 232) vs log (total Th)
- log (Th 230) vs. log (Th 232)

Samples which were outliers from these relationships were identified by analysis of residuals from the linear regression line. Residuals should be approximately normally distributed. Any samples with residuals falling outside the range defined by the mean residual ± 3 SD was considered suspect. In a normal distribution only one in one hundred samples should fall outside this range.

Ion Balance

The net ionic charge of each sample was calculated from the concentrations of major anions and cations. A net charge of zero is expected. A charge frequency distribution was constructed to identify suspect samples. Criteria for identifying supect samples are discussed in Section 3.4.4.

3.0 CHEMICAL RESULTS AND THEIR QUALITY EVALUATION

3.1 Chemical Results for Thorium by Alpha Spectroscopy

The chemical results for thorium isotopes measured by alpha spectroscopy are given in Table 3.1. The sample identifier is that used by Golders (see appendix). Basically, GW stands for groundwater, while SW denotes surface water. Hence, GW-1-B, for example, means GW at Piezometer Nest No. 1, Piezometer No. B. GW-1-B-2 represents one replicate from GW-1-B, while GW-1-B-3 represents a second replicate from GW-1-B. Piezometers GW-1-B, GW-2-V, GW-2-B, GW-02-(VII), GW-03-C, GW-05-C, and surface water sites SW-1 and SW-01 were used for replicate analyses. To aid interpretation of these results, the depth of each piezometer and the measured pH is given in Table 3.1c.

One of the prime concerns of this project is quality assurance. To avoid transcription errors, the laboratory report submitted to BEAK by Monenco Analytical Laboratories (MONENCO; MON) has been directly photographed onto Table 3.1 to present the data.

Table 3.1a represents data measured by Monenco from the first sample submission. After the QA audit of the first submission (see Section 3.4), the second half of the samples were submitted. These results are given in Table 3.1b. In between submittal of the two sets of samples, Monenco moved their laboratory. This delayed obtaining the results; however, care was taken by Monenco to ensure that all instruments were properly functioning and calibrated before analysis commenced for the second submittal. While this delayed the completion of this project, it ensured that quality data were produced from Monenco's point of view.

In addition to the groundwater and surface water samples, GW-Lab-1 and GW-Lab-3 are measurements of the known sample at a low Th-230 activity, while GW-Lab-2 and GW-Lab-4 represent measurements of the known sample made up at a high Th-230 activity. Blank 3 and Blank 4 represent field blanks.

The known samples show some degree of contamination by Th-232 and Th-228. The known samples were created by Becquerel Laboratories (BECQUEREL; BEC) by dissolving high-grade uranium minerals (40 UO_2 by weight) from a northern Saskatchewan mine, cleaning the samples up (adsorption of $ThNO_3^{2-}$ onto an anion exchange resin and

TABLE 3.1a: RADIOISOTOPE MEASUREMENTS FOR LACNOR TAILINGS AREA - FIRST SAMPLE SUBMISSION

	Ra-223	Th-227	Th-228	Th-230	Th-232
GW-1-A		8.0 ± 1.0*	0.28 ± 0.07	0.18 ± 0.05	0.12 ± 0.05
GW-1-B-2		1.5 ± 0.3**	0.31 ± 0.08	0.14 ± 0.05	0.03 ± 0.02
GW-1-B-3		1.0 ± 0.2*	0.14 ± 0.05	0.04 ± 0.02	< 0.005
GW-1-C		6.0 ± 1.0*	0.37 ± 0.10	0.12 ± 0.05	0.07 ± 0.04
GW-1-D		14.0 ± 2.0**	3.5 ± 1.0	100 ± 10	21.0 ± 5.0
GW-1-E		10.0 ± 2.0**	5.4 ± 1.3	46 ± 5	3.2 ± 1.1
GW-2-A		3.0 ± 0.5*	0.22 ± 0.07	0.12 ± 0.05	0.02 ± 0.02
GW-2-B-2	53 ± 5	20.0 ± 3.0**	0.65 ± 0.30	0.32 ± 0.18	< 0.05
GW-2-B-3	58 ± 6	20.0 ± 3.0**	0.40 ± 0.30	0.41 ± 0.30	< 0.05
GW-2-C		33.0 ± 4.0**	1.5 ± 0.8	2.2 ± 0.9	0.21 ± 0.10
GW-2-D			3.5 ± 0.5	23.5 ± 2.0	1.8 ± 0.5
GW-2-i	44 ± 5	14.0 ± 2.0*	1.1 ± 0.3	1.9 ± 0.5	0.08 ± 0.05
GW-2-ii	45 ± 5	20.0 ± 3.0*	1.0 ± 0.2	1.8 ± 0.5	0.14 ± 0.07
GW-2-iii	45 ± 5	16.0 ± 2.0*	2.0 ± 0.5	2.3 ± 0.7	0.14 ± 0.08
GW-2-iv	35 ± 4	13.0 ± 2.0*	1.4 ± 0.3	7.0 ± 1.0	0.77 ± 0.12
GW-2-V-2	26 ± 3	11.5 ± 2.5**	7.2 ± 1.9	177 ± 15	10.0 ± 2.0
GW-2-V-3		9.5 ± 2.0**	7.4 ± 1.4	166 ± 14	14.0 ± 2.0
GW-2-Vi	22 ± 3	11.5 ± 2.5**	29 ± 6	146 ± 12	21.0 ± 4.0
SW-1-2		2.1 ± 0.9**	0.70 ± 0.50	10.3 ± 1.9	0.70 ± 0.50
SW-1-3		3.2 ± 1.0**	0.37 ± 0.12	11.0 ± 1.5	0.64 ± 0.25
GW-Lab-1			0.09 ± 0.02	4.3 ± 0.5	0.04 ± 0.02
GW-Lab-2			0.20 ± 0.03	27.5 ± 2.5	0.10 ± 0.02
Blank 1, GW-Field 1					
Blank 2, GW-Field 2					
Blank 3, GW-Field 3			< 0.005	< 0.005	< 0.005
Blank 4, GW-Field 4			< 0.005	< 0.005	< 0.005

* As of February 19, 1988

** As of February 25, 1988

As of March 7, 1988

TABLE 3.1b: RADIONUCLIDE MEASUREMENTS FOR SECOND SAMPLE SUBMISSION

IDENTIFICATION	Th-228	Th-230	Th-232
	Bq/L	Bq/L	Bq/L
GW 02-(VII)-2	21.8 ± 3.0	194 ± 15	12.5 ± 2.5
GW 02-(VII)-3	17.5 ± 2.0	204 ± 15	17.5 ± 2.0
GW 03-B	0.22 ± 0.03	0.07 ± 0.02	<0.01
GW 03-C-2	0.17 ± 0.02	<0.01	<0.01
GW 03-C-3	0.23 ± 0.03	0.02 ± 0.01	<0.01
GW 03-E	0.17 ± 0.02	0.03 ± 0.01	<0.01
GW 03-F	0.09 ± 0.02	<0.01	<0.01
GW 03-G	0.19 ± 0.03	<0.01	<0.01
GW 04-A2	0.19 ± 0.04	<0.01	<0.01
GW 04-B	0.14 ± 0.03	0.05 ± 0.02	<0.01
GW 04-C	0.18 ± 0.03	<0.01	<0.01
GW 04-D	0.18 ± 0.04	0.08 ± 0.03	<0.01
GW 05-A	0.02 ± 0.01	<0.01	<0.01
GW 05-C-2	0.15 ± 0.03	<0.01	<0.01
GW 05-C-3	0.16 ± 0.03	0.03 ± 0.01	<0.01
GW 05-D	0.19 ± 0.03	<0.01	<0.01
GW 05-F	0.13 ± 0.02	<0.01	<0.01
GW 05-4	0.21 ± 0.03	0.02 ± 0.01	<0.01
SW 02-2	1.2 ± 0.2	19.8 ± 2.0	2.1 ± 0.5
SW 02-3	1.5 ± 0.3	24.0 ± 2.0	1.8 ± 0.5
GW LAB-3	0.02 ± 0.01	5.1 ± 0.5	0.02 ± 0.01
GW LAB-4	0.07 ± 0.04	32 ± 2	0.15 ± 0.07

TABLE 3.1c: DESCRIPTION OF SAMPLE PIEZOMETERS, THEIR DEPTHS AND PORE WATER pH

Piezometer	Depth of Piezometer (m)	pH		Conductance	
		Field	Laboratory	Field	Laboratory
Nest No. 1					
GW-1-A	7.8	5.4	3.4	3,800*	7,700
GW-1-B	11.8	4.5	3.6	7,500*	7,500
GW-1-C	-	6.1	3.7	7,200*	6,810
GW-1-D	-	2.5	2.5	12,700*	6,350
GW-1+E	2.6	2.2	2.0	10,000*	7,730
Nest No. 2					
GW-2-A	16.1	5.4	3.7	1,300*	5,070
GW-2-B	14.5	4.7	3.4	4,500*	7,960
GW-2-C	10.4	3.9	3.7	2,200*	4,030
GW-2-D	-	2.0	2.2	2,200*	5,940
GW-2-i	7.9	3.5	3.4	2,450*	4,180
GW-2-ii	-	4.2	3.7	2,625*	4,570
GW-2-iii	6.6	4.0	3.9	2,200*	3,860
GW-2-iv	5.5	3.8	.5	2,300*	3,870
GW-2-V	3.6	2.0	2.4	4,100*	4,600
GW-2-VI	4.6	1.9	1.95	3,950*	9,690
GW-2-VII	2.6	1.6	1.8	3,800*	11,000
Nest No. 3					
GW-03-B	10.5	7.2	7.4	4,950	4,670
GW-03-C	-	5.6	4.0	6,600	6,370
GW-03-E	6.1	6.5	3.5	5,000	4,310
GW-03-F	4.6	6.5	4.4	5,500	4,290
GW-03-G	3.1	4.2	4.1	6,200	5,010
Nest No. 4					
GW-04-A	11.9	5.3	3.7	4,850	5,370
GW-04-B	-	6.5	4.1	4,550	4,910
GW-04-C	7.3	7.0	6.9	3,750	3,700
GW-04-D	-	6.8	6.2	4,100	3,600

TABLE 3.1c: DESCRIPTION OF SAMPLE PIEZOMETERS, THEIR DEPTHS AND PORE WATER pH

Piezometer	Depth of Piezometer (m)	pH		Conductance	
		Field	Laboratory	Field	Laboratory
Nest No. 5					
GW-05-A	18.3	5.8	3.4	10,750	9,080
GW-05-C	22.1	-	3.6	-	6,630
GW-05-D	10.9	3.2	3.4	6,250	6,460
GW-05-F	8.0	6.0	3.8	4,650	4,440
GW-05-H	6.1	5.3	3.8	5,250	4,870
Surface Water Samples					
SW-01	-	3.2	2.8	4,200	3,600
SW-02	-	2.8	2.7	2,800	2,200

* Field conductivity values measured for these samples are uncertain due to the meter not working well.

then hydroxide coprecipitation), and then measuring the known value. Traces of total thorium in uranium minerals would provide the source of Th-232 and Th-228 given in Table 3.1a and 3.1b.

3.2 Chemical Results for Th-227 and Ra-223

As part of the analysis for Th-228, it was observed that there was some smearing of the peak of Th-228 by Th-227. Accordingly, the first submission of samples were also analyzed by Monenco for Th-227 and its daughter Ra-223.

Inspection of the spectra suggested that resolution of Th-228 from Th-227 was satisfactory (N. Chiu, pers. comm.). Accordingly, the values given in Table 3.1d are a reasonable estimate of activity for Th-227 and Th-228. As an additional aid to interpretation of the data, Becquerel were requested to inspect their thorium spectral records for the QA check samples to estimate Th-227 in addition to Th-228. The results, given in Table 3.1d, indicate that there is reasonable agreement between the two laboratories for both Th-227 and Th-228 given the limitations of the analyses forTh-227 by Becquerel.

As a further check upon the measurements of Th-227, measurements were also made for its daughter Ra-223. Both nuclides are derived from the U-235 decay chain; Th-227 has a decay half-life of 18.2 d and Ra-223 has a decay half-life of 11.43 d. Based upon the short half-life of Ra-223 and the fact that the samples were approximately two months old, it is expected that Ra-223 would be approaching secular equilibrium. Ra-223 activity in the bottle is approximately double that of Th-227 but they are expected to be in secular equilibrium. It is unclear why the samples were not in secular equilibrium. Possible interpretations of these differences include analytical errors made on solutions in secular equilibrium or a groundwater sample which contains much higher concentrations of Ra-223 than Th-227 which have decayed to the levels measured in the sample bottle. The latter explanation is more plausible.

3.3 Chemical Results for Stable Thorium, Cations and Anions

Stable thorium, cations and anions were measured by Barringer. Their methods and a summary of their QA program is given in their report sent to BEAK (see Appendix B.2).

TABLE 3.1d: COMPARISON OF TH-228 AND TH-227 ACTIVITY MEASURED BY TWO LABORATORIES

Sample ID	Th-227 (Bq/L)		Th-228 (Bq/L)	
	Monenco	Becquerel	Monenco	Becquerel
GW-1-B-2	1.5	2 (A)	0.31	0.1
GW-1-B-3	1.0	2 (A)	0.14	0.1
GW-2-B-2	20	20 (A)	0.65	L 0.1
GW-2-B-3	30	20 (A)	0.40	L 0.1
GW-2-V-2	11.5	20 (A)	7.2	6.3
GW-2-V-3	9.5	20 (A)	7.4	6.3
SW-1-2	2.1	2 (A)	0.7	0.1
SW-1-3	3.2	2 (A)	0.37	0.1

L - less than.

A - approximately. Becquerel provided an order of magnitude estimate for Th-227 based upon inspection of the thorium spectra.

The results are tabulated in Table 3.2a and appended in Appendix C due to the large number of pages. Similar to the radionuclide results presented in Table 3.1a, the original report form from Barringer was photographically placed in Table 3.2a to avoid transcription errors.

In addition to the total thorium measurements made by Barringer Laboratories Ltd. (BARRINGER; BAR) using ICP, a few samples were also measured by Elemental Research Inc. (ERI; Table 3.2b) and by the Saskatchewan Research Council (SRC; Table 3.2c). ERI measured three samples using ICP-MS. Methods used, calibration procedures and detection limits are given in the appendix (Appendix B.1). ICP-MS is especially useful for measurements of Th-232. Due to the high activity of Th-230 in two of the three samples, the mass of Th-230 could also be measured with ICP-MS. Th-228 was not detectable by ICP-MS.

Comparison of the different results for total thorium indicate that the majority of results agree at least with another laboratory within a factor of two. The outliers from this qualitative interpretation are the 1.32 ug/L value measured for GW-01-B-2 by ICP-MS (ERI) the difference in values measured colourimetrically (SRC) and by ICP (Barringer) and the values for SW-1-2 measured by ICP. The data are inconclusive concerning the ability of ICP to define realistic values for total thorium. An explanation for why the colourimetric values for GW-02-B are higher than the ICP results while they are lower than the ICP results for SW-1 cannot be given. Each laboratory gives more consistent results on their replicate analysis than in comparison with results from the other laboratory.

An in-depth quantitative treatment of the QA results are presented next in Section 3.4.

3.4 Analysis of Quality Assurance Program for Th-230 Measurements

Five laboratories were used in the Quality Analytical Program of this study for analyses of total thorium and thorium isotope. Monenco (MON) was the prime radionuclide laboratory. Becquerel (BEC) and SRC were the main check laboratories. Barringer (BAR) and Elemental Research Inc. (ERI) were used for specialty analysis. The results from each individual laboratory are given in the plots that follow using the following nomenclature.

TABLE 3.2b: THORIUM MEASUREMENTS BY ICP-MS

Sample	Concentration of Thorium Isotope (ug/L)			
	Th-228	Th-230	Th-232	Th-232 (ICP)*
GW-02-B-2	L 0.005	L 0.005	1.32	680
GW-02-(V)-2	L 0.005	0.18	8,600	3,230
SW-01-3	L 0.005	0.009	123	70

L - less than.

* Measured value by Barringer.

TABLE 3.2c: COMPARISON OF TOTAL THORIUM MEASUREMENTS BY DIFFERENT LABORATORIES

Sample I.D.	Total Thorium Concentrations (ug/L) Measured by: SRC (Colourimetric)	Barringer (ICP)	ERI (ICP-MS)
GW-01-B-2	190	L 50	1.32
GW-01-B-3	30	L 50	-
GW-02-B-2	35	680	-
GW-02-B-3	25	660	-
GW-02-(V)-2	4,100	3,230	8,600
GW-02-(V)-3	4,600	3,210	-
SW-1-2	400	60	-
SW-1-3	310	70	123

L - less than.

Plotting Symbol	Laboratory
1	BAR
2	ERI
3	SRC
4	BEQ
5	MON

The audit of laboratory performance was assessed using three methods:

a. agreement between laboratories,
b. accuracy of each laboratory, and
c. precision within each laboratory.

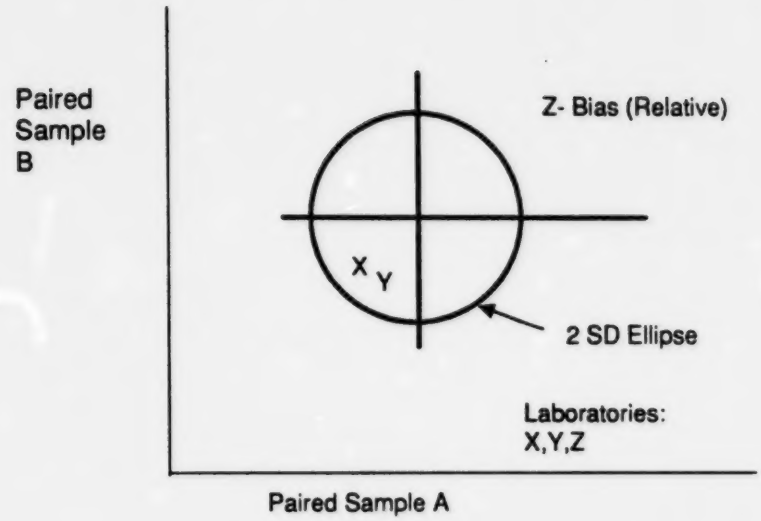
In this study, the accuracy of each laboratory could not be rigorously assessed due to the lack of certified standards.

The agreement between laboratories measures relative bias. It was assessed using Youden Paired Sample Plots which are plots of lab means for one sample versus another sample. The among lab standard deviations for each sample were used to define a 2 SD (Standard Deviation) Ellipse to identify consistent lack of agreement (i.e., relative bias).

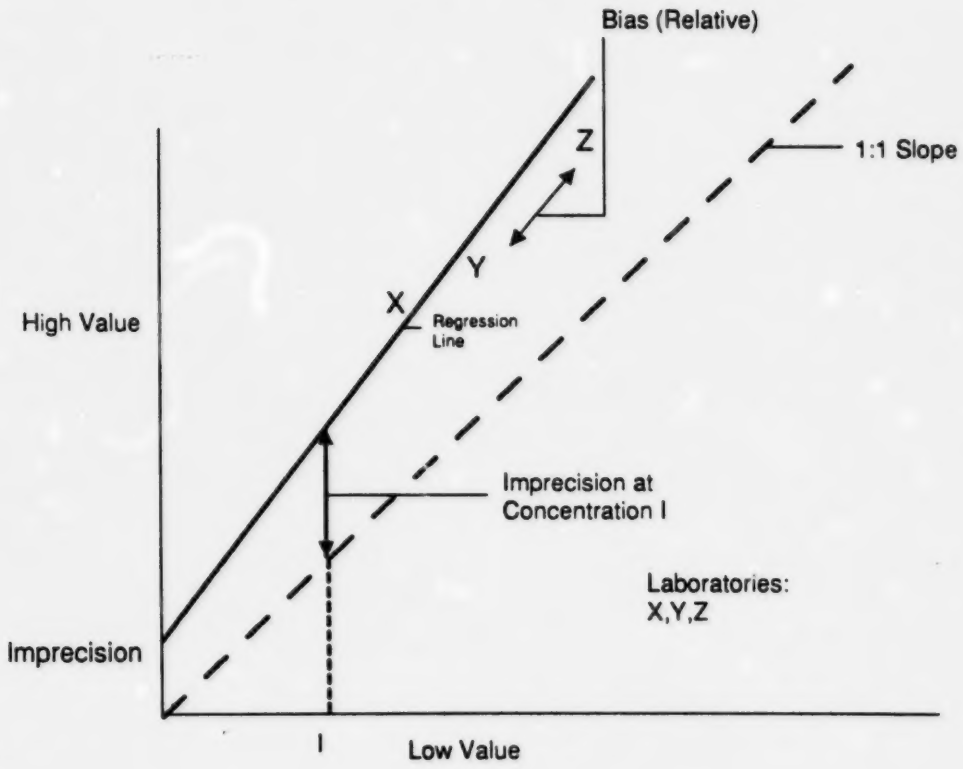
The accuracy of each laboratory was measured relative to target values using synthetic samples. Youden Paired Sample Plots were used to define 2 SD Ellipses, as above. However, with these samples we are better able to state which lab is correct when consistent disagreement is observed. Thus, with these samples we can speak of absolute bias.

The precision within each laboratory was assessed using a duplicate-duplicate plot. This plot is a plot of high versus low duplicate values for a sample. It allows evaluation of change in precision as function of chemical concentration.

These points are diagrammed on the attached figure. With respect to agreement between laboratories, bias is a consistent discrepancy among the laboratories on the sample. Using the values measured by the laboratories, an Ellipse is constructed. Any



A. Youden Plot for Assessing Agreement Between Laboratories and Accuracy in Each Laboratory



B. Duplicate Plot to Assess Precision within Each Laboratory

laboratory lying outside of the Ellipse has a relative bias compared to the other laboratories and would be considered to not agree with the other laboratories. Absolute bias can be assessed if the samples are synthetic and the outlier laboratory (Z) is farthest from the target value.

In this study, it was difficult in most measurements to establish that any laboratory consistently showed a bias in the interlaboratory comparison program. This occured because more than three laboratories are desired to ensure that the 2 SD Ellipse is not strongly influenced by the existence of an outlier laboratory. Three laboratories were not sufficient for this purpose.

Accordingly, the 2 SD Ellipse obtained in this study is likely larger than would result from a study involving more laboratories, and our test for disagreement is rather insensitive. Since there were only three commercial laboratories in Canada that could measure Th-230 at the time that we did this study, a more rigorous definition of the 2 SD Ellipse was not possible.

The method for assessing precision within a laboratory is diagrammed on the attached figure in the form of a duplicate-duplicate plot. The high replicate is plotted versus the low replicate for each replicated sample. The slope of the regression of the high value to low value is compared to that of a perfect fit (the line of 1:1 slope). The intercept describes the high-low difference (imprecision) at low concentrations while the slope of the regression line describes whether the precision is consistent with concentration level or whether precision is a function of concentration level. In the case of the sketch on the attached figure, the slope greater than one indicates that precision varies with concentration.

The regression line can be drawn for each laboratory to represent each lab's precision function. If samples run in duplicate by all laboratories are included in the same plot, an overall within-lab precision function is obtained. When the latter is done, any consistent bias between laboratories on split samples is also apparent. Any consistent displacement of interlaboratory splits, as shown for laboratory versus X and Y on the attached figure, indicates a relative bias.

3.4.1 Analytical Precision - Split Duplicate Samples

First Submission

Duplicate sample results are listed in Table 3.3 for the three main laboratories - SRC, Bequerel and Monenco. These results are illustrated in duplicate - duplicate plots for each chemical parameter. The duplicate-duplicate plots are as follows:

- Figure 3.1: Duplicate-Duplicate Plot for Thorium (Natural);
- Figure 3.2: Duplicate-Duplicate Plot for Th-232;
- Figure 3.3: Duplicate-Duplicate Plot for Th-230;
- Figure 3.4: Duplicate-Duplicate Plot for Th-228; and
- Figure 3.5: Duplicate-Duplicate Plot for Th-227.

Figure 3.1 is presented in the main body; Figures 3.2 to 3.5 inclusive are appended in Appendix C.2.

Of the three main laboratories, only SRC determined total thorium. Figure 3.1 shows the relationship between high and low duplicates. The vertical bar denotes 2 standard deviations computed according to the formula given on page 2.&. The slope of the relationship, b=1.1035 (standard error of b=0.022), is significantly greater than 1 (p less than 0.05) indicating that analytical variability increases with concentration. This is not an unusual property of analytical systems. Over the concentration range of the study the standard deviation of thorium determination ranged up to approximately 0.3 mg/L or about 10% of the reported concentration.

Figure 3.2 shows the duplicate-duplicate plot for Th232. The best precision (i.e., lowest spread of duplicate results) was achieved by Becquerel, with a 1:1 relationship between duplicates (slope of plots BEQ 1.0; SRC 1.2; MON 1.4). Both Monenco and SRC suggest increasing analytical variability with increasing concentration over the study range (slope greater than 1.0). For the group as a whole, the standard deviation of Th-232 determination ranged up to approximately 3 Bq/L or about 15% (relative standard deviations; RSD) of the reported concentration.

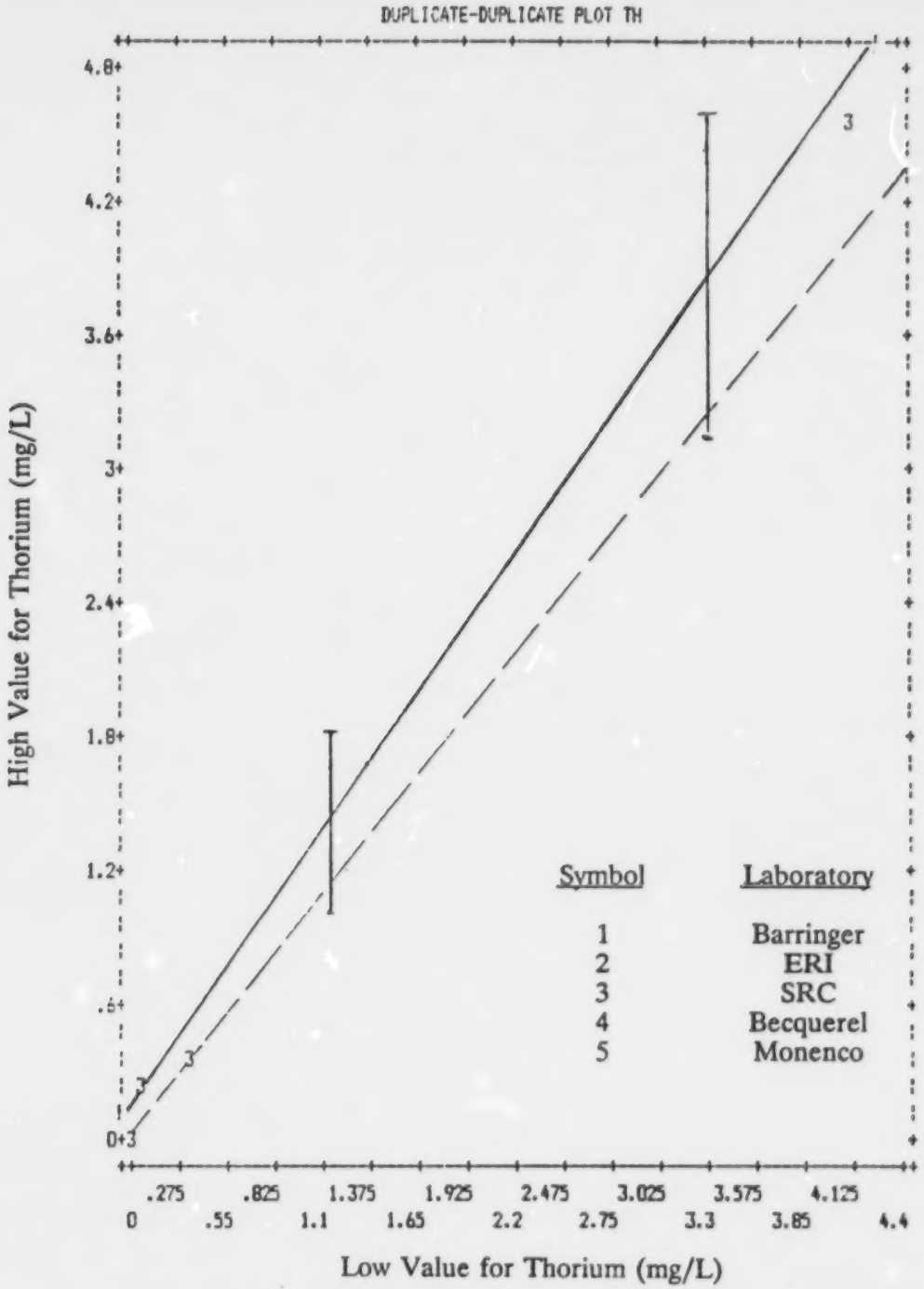


FIGURE 3.1: DUPLICATE-DUPLICATE PLOT FOR THORIUM
(dashed line represents perfect precision, solid line SRC)

TABLE 3.3: DUPLICATE SAMPLE RESULTS FOR THREE MAIN LABORATORIES (first submission)

Lab	Lab No.	Par. (Bq/L)	Rep. 2 GW1B	Rep. 3 GW1B	Rep. 2 GW2B	Rep. 3 GW2B	Rep. 2 GW2V	Rep. 3 GW2V	Rep. 2 SW1	Rep. 3 SW1
SRC	3	Th (mg/L)	0.19	0.03	0.035	0.025	4.1	4.6	0.4	0.31
SRC	3	Th-232	0.77	0.12	0.14	0.1	20	25	2.5	1.7
SRC	3	Th-230	*	*	*	*	90	80	8	7.5
SRC	3	Th-228	*	*	*	*	*	*	*	*
BEQ	4	Th-232	0.007	0.007	0.015	0.08	13	13	0.68	0.64
BEQ	4	Th-230	0.18	0.27	LT0.1	LT0.1	200	210	9.6	9.5
BEQ	4	Th-228	0.1	0.1	LT0.1	LT0.1	6.3	6.3	0.1	0.1
BEQ	4	Th-227	2	2	20	20	20	20	2	2
MON	5	Th-232	0.03	LT0.005	LT0.005	LT0.005	10	14	0.71	0.64
MON	5	Th-230	0.14	0.04	0.32	0.41	177	166	10.3	11
MON	5	Th-228	0.31	0.14	0.65	0.41	7.2	7.4	0.71	0.37
MON	5	Th-227	1.5	1	20	20	11.5	9.5	2.1	3.2

* = no result reported

While the precision of SRC was quite comparable to that of the other laboratories, a high bias was suggested, particularly at the upper end of the study range, where the concentrations reported by SRC were about double those reported by other laboratories. This is evident from Figure 3.2 since both high and low duplicates for SRC exceeded the highest values of other laboratories on the high concentration sample. It is also evident from paired sample results (Section 3.4.3). However, with only three participating laboratories, a significant bias is difficult to detect. Moreover, since the samples for duplicate analysis were not synthetically prepared with target concentrations, a relative rather than absolute bias is suggested.

Figure 3.3 shows the duplicate-duplicate plot for Th-230. Precision is quite good, and quite comparable among laboratories. For the group as a whole, the standard deviation of Th-230 determination ranged up to approximately 14 Bq/L or 7% (RSD) of the reported concentration. However, a low bias by SRC was suggested at the upper end of the study range, where SRC reported concentrations which were less than half those reported by other laboratories.

Figure 3.4 shows the duplicate-duplicate plot for Th-228, which was determined only by Becquerel and Monenco. Precision was relatively constant with concentration, and similar among laboratories, with a standard deviation of approximately 0.14 Bq/L for the group as a whole. Figure 3.5 illustrates similar results for Th-227, with a standard deviation of approximately 0.35 Bq/L over the study range.

Second Submission

Duplicate sample results for the second set of samples are listed in Table 3.4 for the three main laboratories - SRC, Bequerel and Monenco. These were the only laboratories participating during the second round of analyses. The results are illustrated in duplicate-duplicate plots, and the precision achieved is compared between submissions.

The duplicate-duplicate results for the second submission are presented graphically as follows:

- Figure 3.6: Duplicate-Duplicate Plot for Th-232;
- Figure 3.7: Duplicate-Duplicate Plot for Th-230; and
- Figure 3.8: Duplicate-Duplicate Plot for Th-228.

TABLE 3.4: DUPLICATE SAMPLE RESULTS FOR THREE MAIN LABORATORIES (second submission)

Lab	Lab No.	Par. (Bq/L)	Rep. 2 GW2VII	Rep. 3 GW2VII	Rep. 2 GW3C	Rep. 3 GW3C	Rep. 2 GW5C	Rep. 3 GW5C	Rep. 2 SW2	Rep. 3 SW2
SRC	3	Th-232	18	20	LT0.04	LT0.04	LT0.04	LT0.04	3.0	3.5
SRC	3	Th-230	190	200	0.07	0.07	LT0.04	LT0.04	20	25
SRC	3	Th-228	20	19	0.20	0.19	0.19	0.18	2.5	2.5
BEQ	4	Th-232	11.6	11.0	LT0.02	LT0.02	LT0.01	LT0.01	1.50	1.46
BEQ	4	Th-230	172	176	0.79	0.12	0.08	0.10	20.7	20.8
BEQ	4	Th-228	9.2	10.2	0.37	0.27	0.05	0.08	0.92	0.97
MON	5	Th-232	12.5	17.5	LT0.01	LT0.01	LT0.01	LT0.01	2.1	1.8
MON	5	Th-230	194	204	LT0.01	0.02	LT0.01	0.03	19.8	24.0
MON	5	Th-228	21.8	17.5	0.17	0.23	0.15	0.16	1.2	1.5

LT = less than

Figure 3.6 is presented in the main body; Figures 3.7 and 3.8 are appended in Appendix C.2

Figure 3.6 shows the duplicate-duplicate plot for Th-232 in the second submission. As in the first submission, Becquerel had the highest precision and Monenco had the lowest precision. For the group as a whole, the standard deviation of Th-232 determinations ranged up to approximately 3 Bq/L or about 15% (RSD) of the reported concentration, similar to the precision achieved in the first submission. SRC determinations were not as significantly higher than the other laboratories as in the first submission, although SRC still has the highest values.

Figure 3.7 shows the duplicate-duplicate plot for Th-230 in the second submission. There was little difference in precision between laboratories. For the group as a whole, the standard deviation of Th-230 determination ranged up to approximately 11 Bq/L, or about 6% (RSD) of the reported concentration. This precision is similar to that achieved in the first submission.

Figure 3.8 shows the duplicate-duplicate plot for Th-228. The concentration range of Th-228 in split samples appeared to be higher in the second submission than the first. The standard deviation of Th-228 determination for the group as a whole ranged up to approximately 3 Bq/L, or about 15% (RSD) of the reported concentration. These results differ from those of the first submission, suggesting less precision, possibly due to the higher concentration range of the evaluation.

3.4.2 Isotope Ratios

First Submission

Outlier samples or laboratories can sometimes be identified from relationships between different constituents measured in the same samples. Consistent relationships are expected between Th-232 and Th, (Figure 3.9) and between Th-230 and Th (Figure 3.10). However, only SRC determined both isotopes and stable Th.

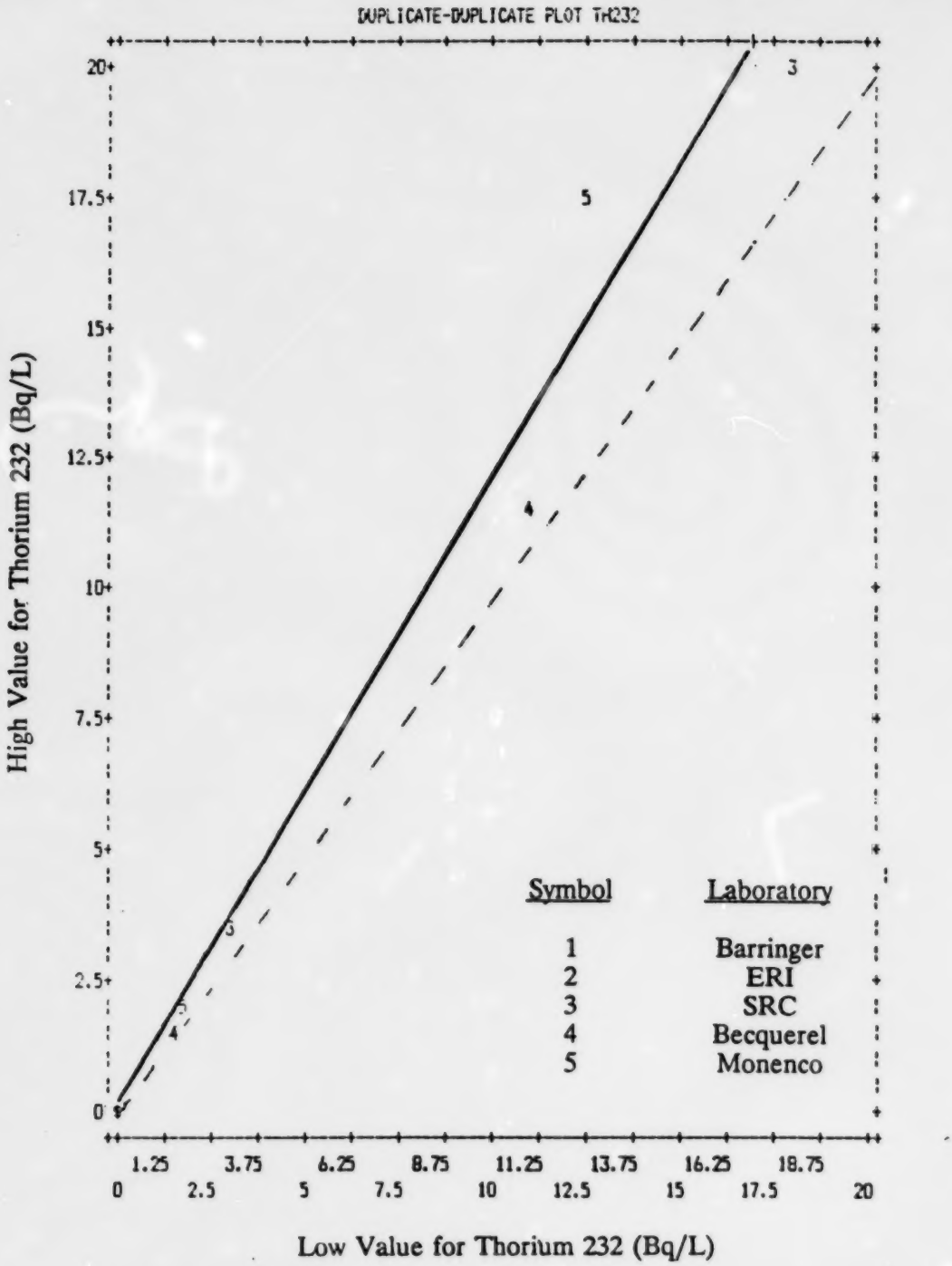
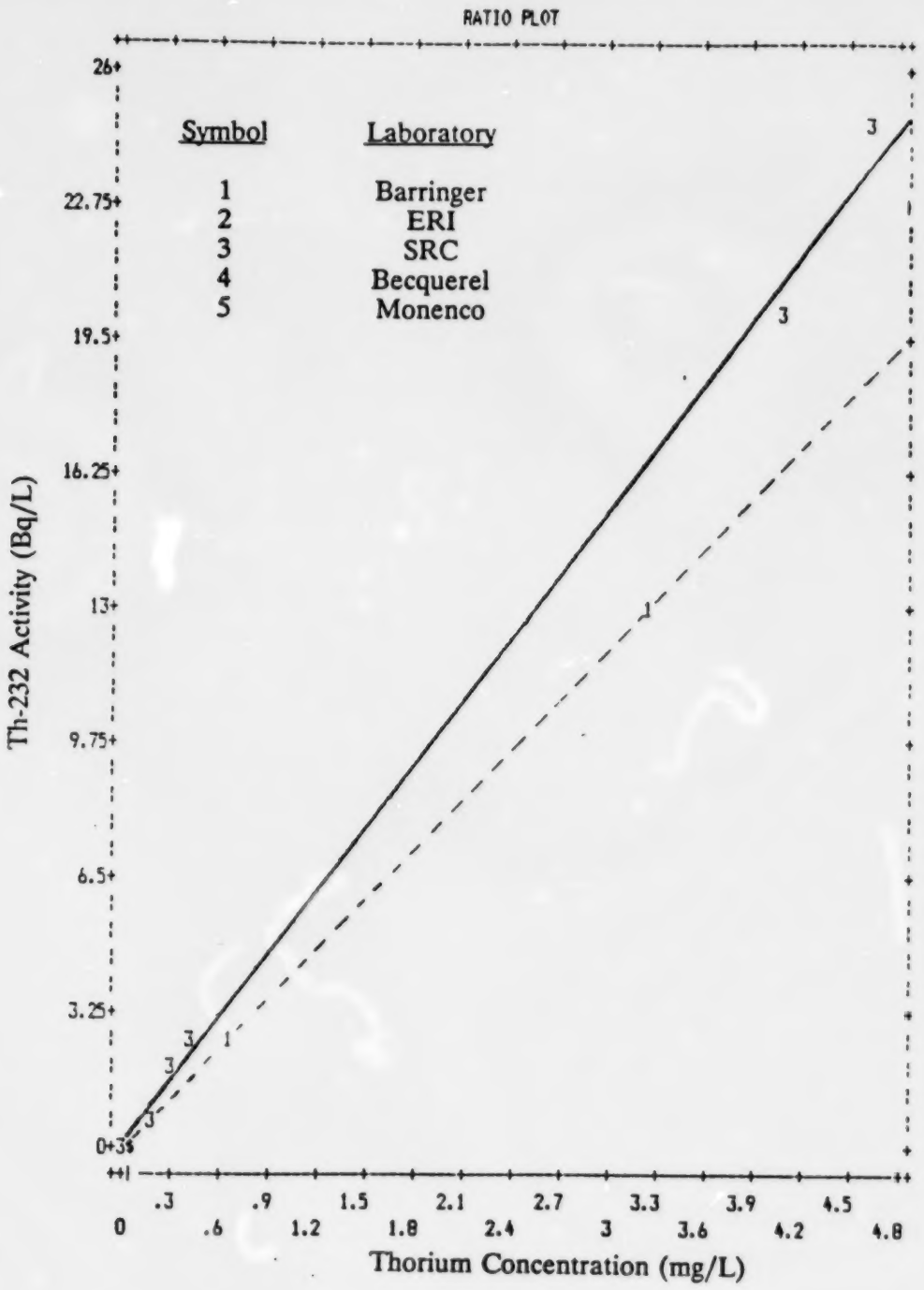
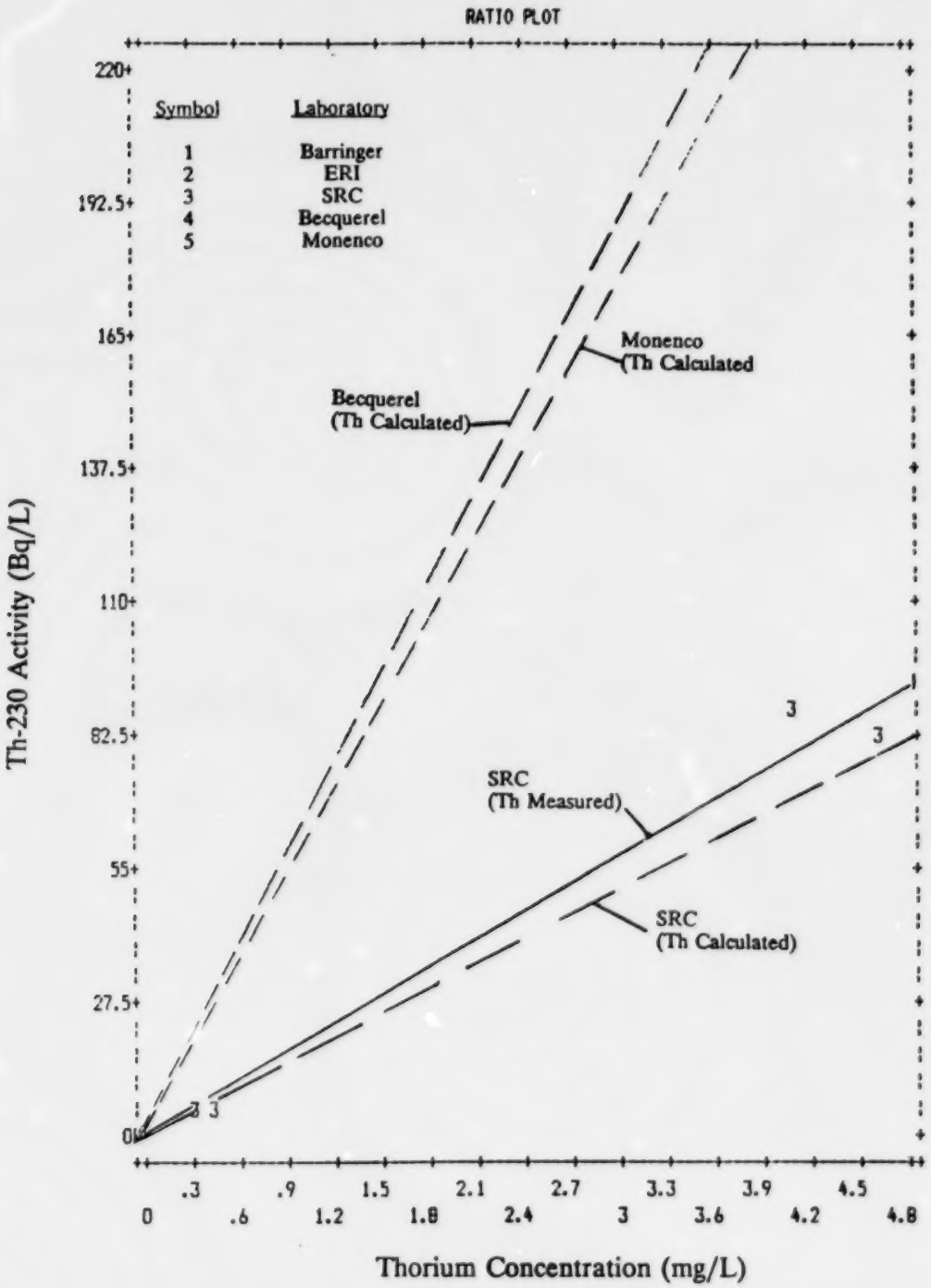


FIGURE 3.6: DUPLICATE-DUPLICATE PLOT FOR TH-232
(solid line represents the group of three main laboratories, dashed line perfect precision)



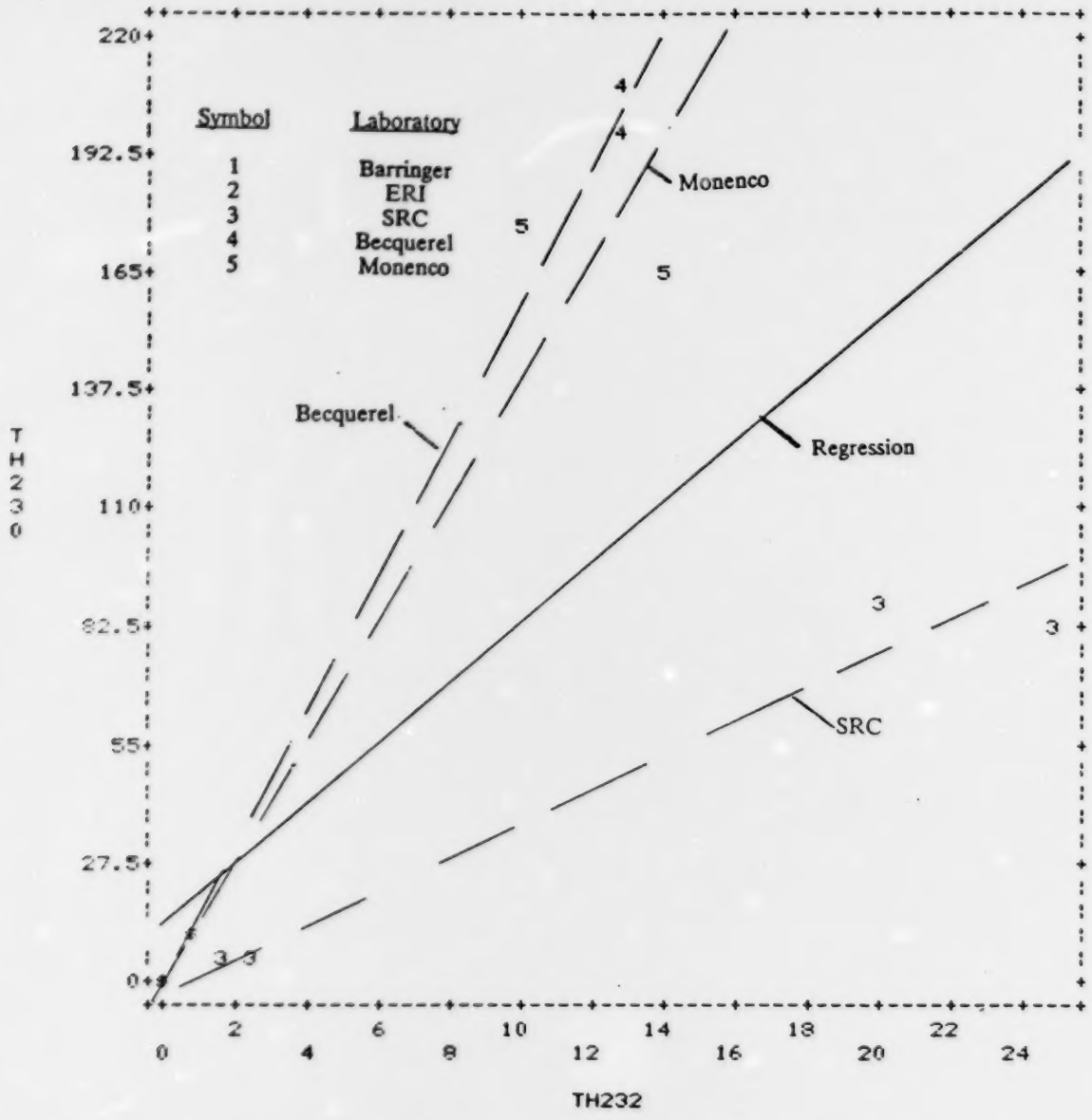
16 cases plotted. Regression statistics of TH232 on TH:
Correlation .98886 R Squared .97784 S.E. of Est 1.23305 2-tailed Sig. .0000
Intercept(S.E.) -.17310(.37571) Slope(S.E.) 4.82596(.19416)
Use first digit of LABNO as plotting symbol and $ for multiple occurrence.

FIGURE 3.9: RATIO PLOT OF TH-232 VS. THORIUM
(dashed line represents expected ratio , solid line SRC)



4 cases plotted. Regression statistics of TH230 on TH:
Correlation .98386 R Squared .96799 S.E. of Est 9.81463 2-tailed Sig. .0161
Intercept(S.E.) 1.61261(7.56412) Slope(S.E.) 19.02759(2.44686)
Use first digit of LABNO as plotting symbol and * for multiple occurrence.

Figure 3.10A: RATIO PLOT OF TH-230 VS. THORIUM CONCENTRATION
For plotting Th-230 values, the activity measured by each laboratory was used. For plotting Thorium values, total Th measured by SRC was used for solid line while dashed lines was for total Th calculated from measured Th-232 activity.



20 cases plotted. Regression statistics of TH230 on TH232:
Correlation .73671 R Squared .54274 S.E. of Est 52.84975 Sig. .0002
Intercept(S.E.) 12.26821(14.24378) Slope(S.E.) 7.20513(1.55880)
Use first digit of LAB as plotting symbol and $ for multiple occurrence.

Figure 3.10B: Ratio Plot of Th-230 versus Th-232 for first submission

Figure 3.9 suggests that SRC is overestimating Th-232 relative to the theoretical expectation, at least at the higher concentrations in the study range. Figure 3.10 suggests that SRC is underestimating Th-230. These results are consistent with the implications of the inter-laboratory comparison.

Second Submission

No laboratory determined both Th and a thorium isotope in the second submission. Consequently, Th isotopes 230 and 232 were plotted against each other, rather than against total thorium. Since most of the Th mass is Th-232, the Th-232 axis can be expressed in calculated Th units for comparison to the Th-230:Th plot from the first submission.

The Th-230:232 ratio plot in Figure 3.11 does not show obvious overestimation of Th-232 (or underestimation of Th-230) as was suggested in the first submission. While the SRC ratio still slightly favours Th-232 relative to the ratio in the other laboratories, SRC measurements no longer deviate so clearly as in Figure 3.10. Any differences which exist between laboratories are primarily on the Th-232 axis.

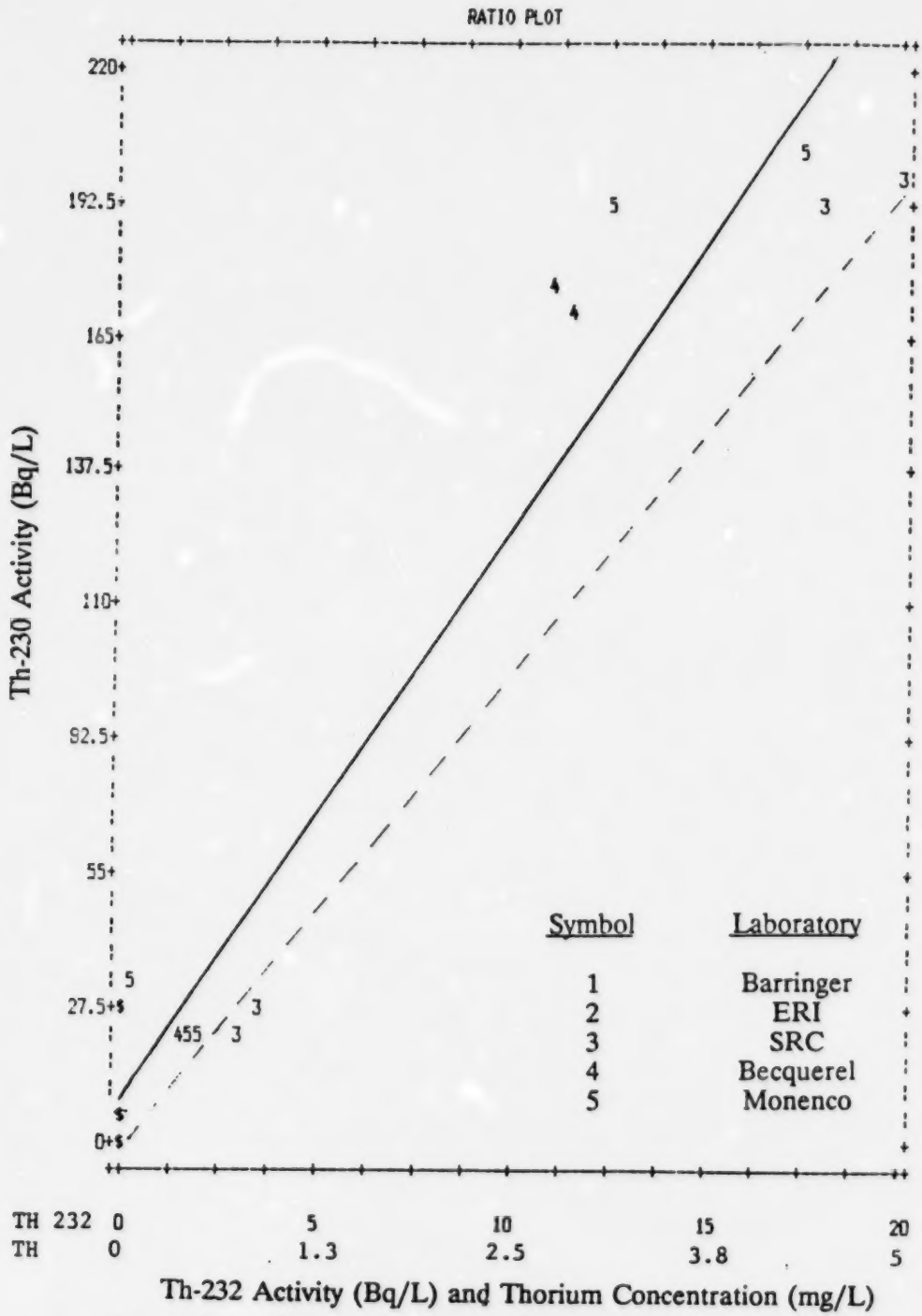
3.4.3 Analytical Bias - Paired Sample Plots

First Submission

Table 3.5 shows mean sample results for each laboratory on each chemical parameter. These results are illustrated in Youden paired sample plots for identification of biased laboratories. In each plot, 2 inter-laboratory standard deviations are indicated by crossbars, and laboratories outside this range are considered outliers.

Graphs of the Youden paired plots for examining bias in the first submission are presented as follows:

- Figure 3.12: Paired Sample Plot of Th-232 in Synthetic Samples GWLAB1 and GWLAB2;
- Figure 3.13: Paired Sample Plot of Th-230 in Synthetic Samples GWLAB1 and GWLAB2;



30 cases plotted. Regression statistics of TH230 on TH232:
Correlation .96883 R Squared .93863 S.E. of Est 18.65643 2-tailed Sig. 0.0
Intercept(S.E.) 5.33689(3.92578) Slope(S.E.) 11.58426(.55980)
Use first digit of LABNO as plotting symbol and $ for multiple occurrence.

FIGURE 3.11: RATIO PLOT OF TH-230 VS. TH-232
(solid line represents the group of three main laboratories, dashed line SRC)

TABLE 3.5: MEAN SAMPLE RESULTS FOR PARTICIPATING LABORATORIES (first submission)

Lab	Lab No.	Par. (Bq/L)	GWLAB1	GWLAB2	GW1B	GW2B	GW2V	SW1
BAR	1	Th (mg/L)	*	*	LT0.05	0.67	3.22	0.065
BAR	1	Th-232	*	*	LT0.2	2.7	13	0.26
BRN	2	Th-232	*	*	*	0.0052	3.3	0.5
BRN	2	Th-230	*	*	*	LT0.7	129	6.5
SRC	3	Th (mg/L)	*	*	0.11	0.03	4.35	0.355
SRC	3	Th-232	0.06	0.04	0.45	0.12	23	2.1
SRC	3	Th-230	5	30	*	*	85	7.8
SRC	3	Th-228	LT0.02	0.03	*	*	*	*
BEQ	4	Th-232	LT0.007	LT0.009	0.007	0.048	13	0.66
BEQ	4	Th-230	5.2	31	0.23	0.1	205	9.55
BEQ	4	Th-228	LT0.01	LT0.01	0.1	0.1	6.3	0.1
BEQ	4	Th-227	LT0.1	LT0.1	2	20	20	2
MON	5	Th-232	0.04	0.1	0.018	0.005	12	0.68
MON	5	Th-230	4.3	27.5	0.09	0.37	172	10.7
MON	5	Th-228	0.2	0.2	0.45	0.53	7.3	0.54
MON	5	Th-227	*	*	1.3	20	10.5	2.7

* = no result reported

- Figure 3.14: Paired Sample Plot of Th-232 in Natural Samples GW1B and SW1;
- Figure 3.15: Paired Sample Plot of Th-232 in Natural Samples GW2D and SW1;
- Figure 3.16: Paired Sample Plot of Th-232 in Natural Samples GW2V and SW1;
- Figure 3.17: Paired Sample Plot of Th-230 in Synthetic Samples GWLAB1 and GWLAB2;
- Figure 3.18: Paired Sample Plot of Th-230 in Natural Samples GW2V and SW1; and
- Figure 3.19: Paired Sample Plot of Th-228 in Synthetic Samples GWLAB1 and GWLAB2.

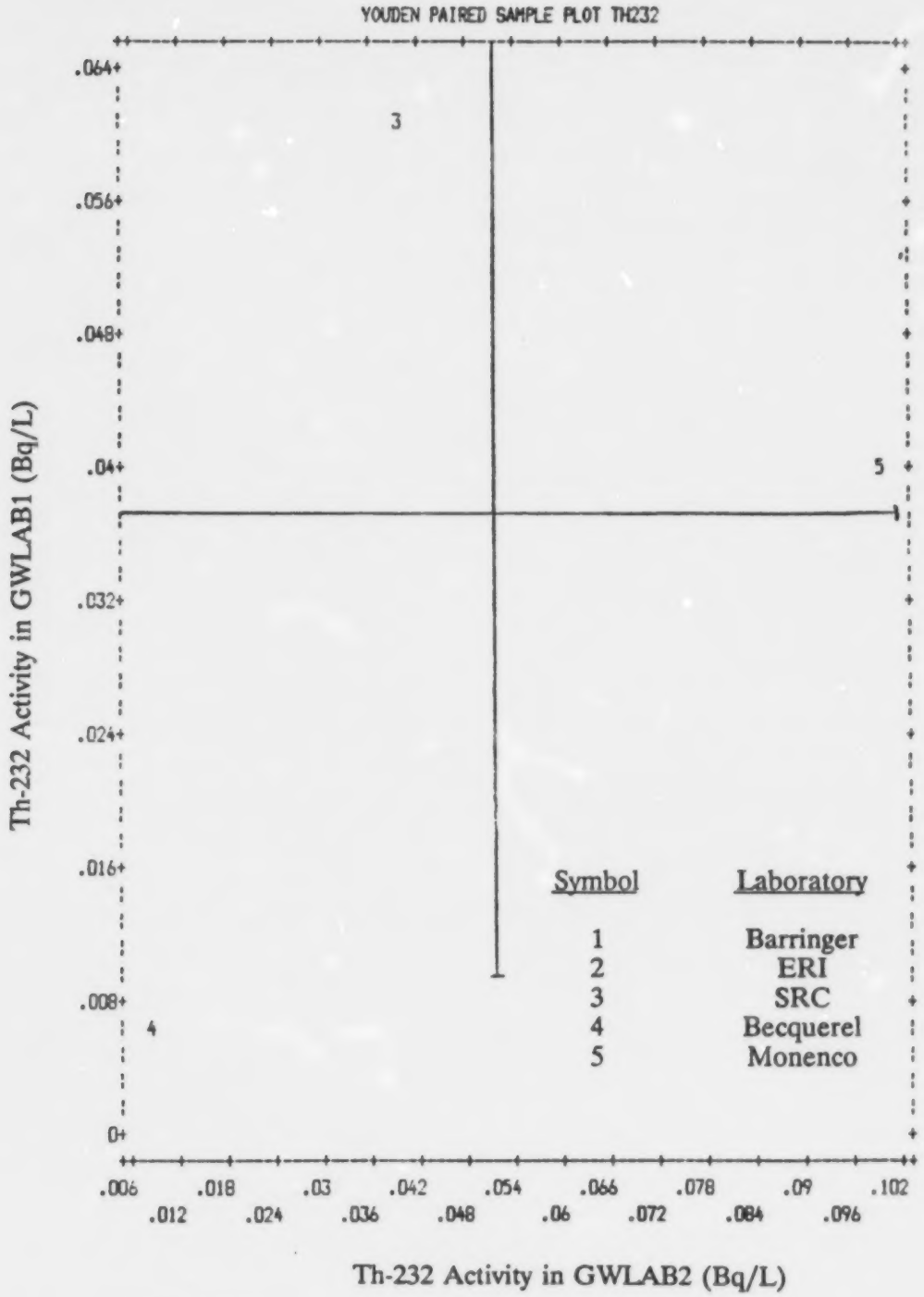
Figure 3.12 is presented in the main body; figures 3.13 to 3.19 inclusive are appended (Appendix C.2).

An absolute bias can only be determined when the true sample concentration is known. In synthetic samples a target concentration is known, although this is not as reliable as the proven concentration of a reference standard. In this study, sufficient isotope was available for synthetic sample preparation only at the lower end of the concentration range.

Figure 3.12 shows the Youden paired sample plot for Th-232 in the synthetic samples GWLAB1 and GWLAB2. This plot shows reasonable agreement between the three main laboratories at low concentrations. Figure 3.13 shows similar agreement for Th-230 in the same synthetic samples, GWLAB1 and GWLAB2, with target concentrations of 4.6 and 29 Bq/L Th-230.

Figure 3.14 shows the paired sample plot for Th-232 in the natural samples GW1B and GW2V. A high bias is suggested for SRC which lies above the 1SD range on both samples. However, with a small number of participating laboratories the interlaboratory standard deviation itself is quite sensitive to an individual laboratory bias, and this reduces the sensitivity of the test. In large studies, the 2SD range is usually used as a test criterion for outlier laboratories, and SRC does not fall outside this limit.

Figure 3.15 shows the paired sample plot for Th-232 in natural samples GW1B and SW1. Again a high bias is suggested for SRC, which falls just outside the 2SD limit. Only one in twenty laboratories would be expected to fall outside this limit in a population of comparable laboratories.



3 cases plotted.
Use first digit of LABNO as plotting symbol and * for multiple occurrence.

FIGURE 3.12: PAIRED SAMPLE PLOT OF TH-232 IN SYNTHETIC SAMPLES GWLAB1 AND GWLAB2 (crossbars show interlaboratory SD)

Figure 3.16 shows the paired sample plot for Th-232 in natural samples GW2V and SW1. In addition to the three main laboratories, two other laboratories were included here (Bob Brown, Elemental Research Inc., using an ICP-MS technique, and Barringer, reporting Th from which Th-232 was calculated). Again, a high bias is suggested for SRC.

Figure 3.17 shows the Youden paired sample plot for Th-232 in the natural samples GW2B and SW1. This shows erratic performance for SRC (high on SW1 but not GW2B) and for Barringer (high on GW2B but not on SW1).

Figure 3.18 shows the paired sample plot for Th-230 in the natural samples GW2V and SW1. Both SRC and Elemental Research appear to be lower than Monenco and Becquerel. However, because of the small number of participating labs, and the high interlaboratory standard deviation, these differences are not significant.

Since SRC did not report Th-230 for the other natural samples, no other Youden plots are illustrated. In general, Monenco and Becquerel were in good agreement.

Figure 3.19 shows the Youden paired sample plot for Th-228 in the synthetic samples GWLAB1 and GWLAB2. All three laboratories are in reasonable agreement, all within the 2SD limit, although Monenco was twice as high as SRC and Becquerel.

Second Submission

Table 3.6 shows mean sample results for each laboratory on each chemical parameter, during the second sample submission. Youden paired sample plots illustrate the extent of agreement between laboratories. All three participating laboratories were consistently within 2 SD of the interlaboratory mean.

Youden paired sample plots to examine analytical bias for the second submission are presented in the following figures.

- Figure 3.20: Paired Sample Plot of Th-232 in Synthetic Samples GWLAB3 and GWLAB4;
- Figure 3.21: Paired Sample Plot of Th-232 in Natural Samples GW2VII and GW3C;

TABLE 3.6: MEAN SAMPLE RESULTS FOR PARTICIPATING LABORATORIES (second submission)

Lab	Lab No.	Par. (Bq/L)	GWLAB3	GWLAB4	GW2VII	GW3C	GW5C	SW2
BAR	1	Th (mg/L)	-	-	2.81	LT0.05	LT0.05	0.37
BAR	1	Th-232	-	-	11.24	LT0.2	LT0.2	1.48
SRC	3	Th-232	LT0.04	0.10	19	LT0.04	LT0.04	3.3
SRC	3	Th-230	5.0	30	195	0.07	LT0.04	22.5
SRC	3	Th-228	LT0.04	LT0.04	19.5	0.20	0.19	2.5
BEQ	4	Th-232	LT0.02	LT0.05	11.3	LT0.02	LT0.01	1.48
BEQ	4	Th-230	4.44	27.6	174	0.46	0.09	20.8
BEQ	4	Th-228	0.07	0.07	9.7	0.32	0.07	0.95
MON	5	Th-232	0.02	0.15	15.0	LT0.01	LT0.01	2.0
MON	5	Th-230	5.1	32	199	LT0.02	LT0.02	22.1
MON	5	Th-228	0.02	0.07	19.7	0.20	0.16	1.4

- Figure 3.22: Paired Sample Plot of Th-232 in Natural Samples GW2VII and GW5C;
- Figure 3.24: Paired Sample Plot of Th-232 in Natural Samples GW3C and GW5C;
- Figure 3.25: Paired Sample Plot of Th-232 in Natural Samples GW3C and SW2;
- Figure 3.26: Paired Sample Plot of Th-232 in Natural Samples GW5C and SW2;
- Figure 3.27: Paired Sample Plot of Th-230 in Synthetic Samples GWLAB3 and GWLAB4;
- Figure 3.28: Paired Sample Plot of Th-230 in Natural Samples GW2VII and GW3C;
- Figure 3.29: Paired Sample Plot of Th-230 in Natural Samples GW2VII and GW5C;
- Figure 3.30: Paired Sample Plot of Th-230 in Natural Samples GW2VII and SW2;
- Figure 3.31: Paired Sample Plot of Th-230 in Natural Samples GW3C and GW5C;
- Figure 3.32: Paired Sample Plot of Th-230 in Natural Samples GW3C and SW2;
- Figure 3.33: Paired Sample Plot of Th-230 in Natural Samples GW5C and SW2;
- Figure 3.34: Paired Sample Plot of Th-228 in Synthetic Samples GWLAB3 and GWLAB4;
- Figure 3.35: Paired Sample Plot of Th-228 in Natural Samples GW2VII and GW3C;
- Figure 3.36: Paired Sample Plot of Th-228 in Natural Samples GW2VII and GW5C;
- Figure 3.37: Paired Sample Plot of Th-228 in Natural Samples GW2VII and SW2;
- Figure 3.38: Paired Sample Plot of Th-228 in Natural Samples GW3C and GW5C;
- Figure 3.39: Paired Sample Plot of Th-228 in Natural Samples GW3C and SW2; and
- Figure 3.40: Paired Sample Plot of Th-228 in Natural Samples GW5C and SW2.

A representative figure (Fig. 3.20) is presented in the main body; the remainder (Figures 3.21 to 3.40 inclusive) are appended.

While no significant interlaboratory differences were detected, tests based on only three participants have limited power. Figure 3.20 illustrates good agreement on Th-232 content of synthetic samples GWLAB3 and GWLAB4. Figures 3.21 through 3.26 show SRC consistently in the upper right quadrant for Th-232 determination in natural samples, just outside the 1 SD limit. Thus a slight, though non-significant, overestimation of Th-232 by SRC is still suggested. This was less pronounced than during the first sample submission.

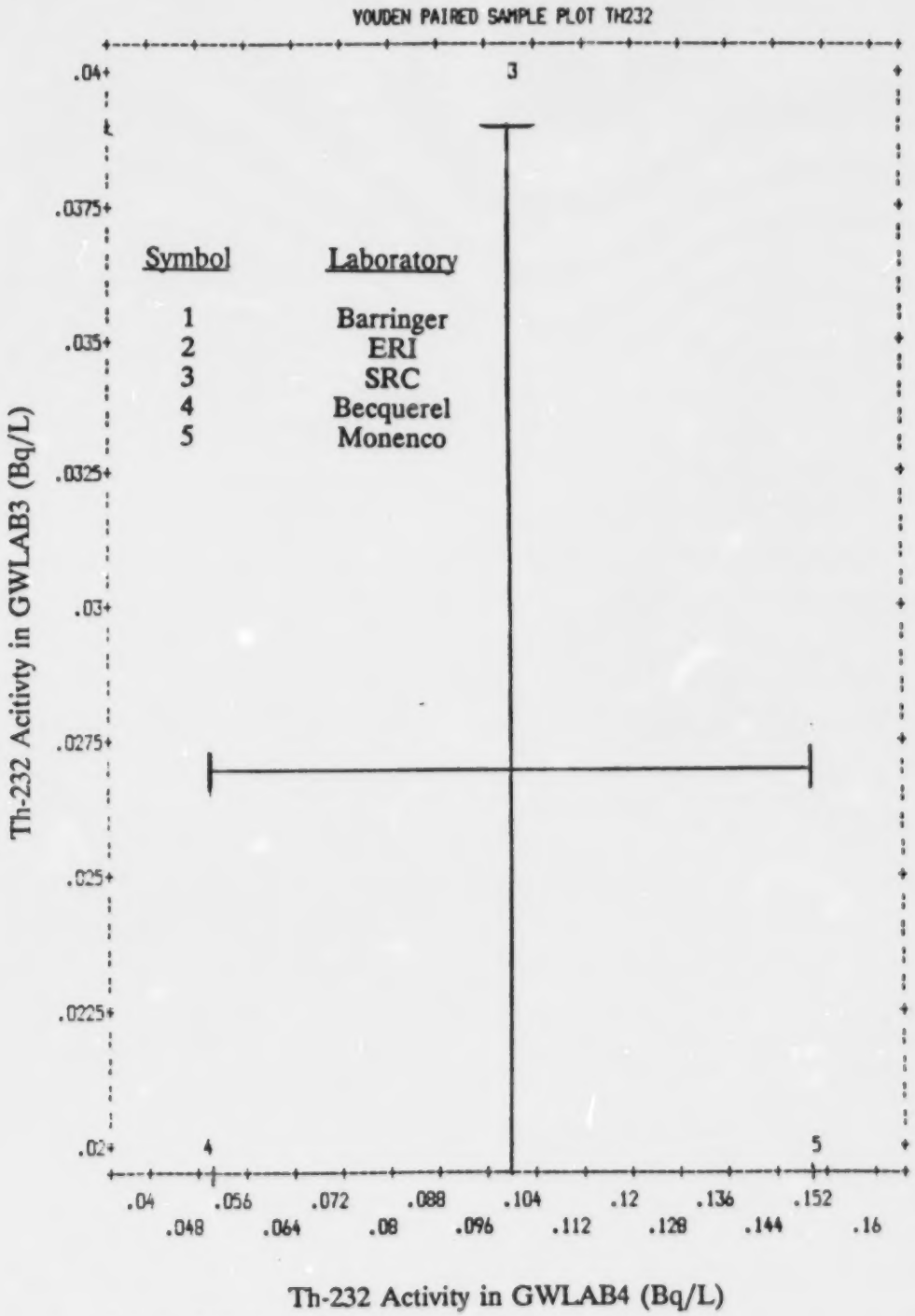


FIGURE 3.20: PAIRED SAMPLE PLOT OF TH-232 IN SYNTHETIC SAMPLES GWLAB3 AND GWLAB4 (crossbars show inter-laboratory SD)

Figure 3.27 illustrates agreement on Th-230 in synthetic samples GWLAB3 and GWLAB4. Figures 3.28 through 3.33 show no consistent interlaboratory pattern for Th-230 in natural samples, and no evidence of Th-230 underestimation by SRC as suggested during the first sample submission.

Figure 3.34 illustrates agreement on Th-228 in synthetic samples GWLAB3 and GWLAB4. Figures 3.35 through 3.40 show no consistent interlaboratory pattern for Th-228 in natural samples, and no discrepancies outside the 2 SD limit. Thus, there is no evidence of interlaboratory bias on this parameter.

3.4.4 Cation Anion Balance

The major cations and anions which contribute to the charge balance are listed in Table 3.7. The lab cation balance is calculated based upon lab measured pH's while field cation balances are calculated, based upon field pH measurements. The comparison is expressed as a relative fraction (cation-anion/anion, entitled "frac anion") and as a cation/anion ratio (entitled "cation ratio"). A perfect balance would result in a value of zero for the relative fraction, and a value of 1.0 for the cation/anion ratio.

The results indicate that the lab-based measurements, on average, are within acceptable standards (10%) although a cation anion balance of 5% is ideal. The highest charge deviation was 26%. Approximately half the samples, individually, were outside the 10% limit. The cation charge is consistently lower than that of the sulphate (anion) charge. In establishing the cation balance, it was assumed that iron was in the reduced state (plus 2 charge). If a substantive fraction of the iron were in a plus three state, the charge balance would close. It is difficult, however, to conclude that such a large portion of iron would be III in reduced pore water of the tailings. Other cations could be included, but they do not make a substantial contribution to electoneutrality.

3.5 Summary of Findings from Quality Assurance Program

3.5.1 Structure of Program

A quality assurance program was established for field, sample handling and shipment, and laboratory components in resampling Th-230 in the Lacnor Tailings management area.

TABLE 3.7: CATION-ANION BALANCES FOR LACNOR PORE WATER DATA

T7-4721A 04/02/88

SAMPLE ID	AL MG/L	CA MG/L	FE MG/L	K MG/L	MG MG/L	MN MG/L	NA MG/L	ZN MG/L	PH LAB	PH FIELD	SO4= MG/L	LAB CATION MEQ/L	FIELD CATION MEQ/L	ANION MEQ/L	LAB FRAC ANION	FIELD FRAC ANION	LAB CAT/AN RATIO	FIELD CAT/AN RATIO
GW01-A	3.53	376	2900	88.6	162	15.5	27.4	0.22	3.41	5.4	8480	140.653	140.268	176.483	-0.20	-0.21	0.80	0.79
GW01-B-2	2.1	391	3160	106	158	17.4	25.6	0.34	3.53	4.5	8350	150.561	150.298	173.777	-0.13	-0.14	0.87	0.86
GW01-B-3	2.16	405	3200	108	164	17.5	25.9	0.35	3.6	4.5	8020	153.215	152.996	166.909	-0.08	-0.08	0.92	0.92
GW01-C	13.9	417	2650	92	148	13.9	18.2	0.37	3.69	6.1	7400	133.202	132.998	154.006	-0.14	-0.14	0.86	0.86
GW01-D	163	433	1160	82.9	65	0.67	3.4	0.31	2.47	2.5	5080	92.250	92.024	105.723	-0.13	-0.13	0.87	0.87
GW01-E	83.8	462	792	43.2	15.7	0.26	1.5	0.13	2.04	2.2	4300	72.286	69.475	89.490	-0.19	-0.22	0.81	0.78
GW02-A	1.38	417	1690	56.4	111	11.9	10.3	0.14	3.68	5.4	4480	93.089	92.884	93.236	-0.00	-0.00	1.00	1.00
GW02-B-2	25.5	387	3100	118	181	17.4	38	0.74	3.44	4.7	9040	153.634	153.291	188.137	-0.18	-0.19	0.82	0.81
GW02-B-3	24.6	396	3080	117	180	17.7	38.3	0.71	3.51	4.7	9080	152.630	152.341	188.970	-0.19	-0.19	0.81	0.81
GW02-C	78.1	448	915	29.2	40	0.82	6.9	3.14	3.66	3.9	3620	68.443	68.350	75.338	-0.09	-0.09	0.91	0.91
GW02-D	90.7	430	576	22.1	10.9	0.28	1.1	0.11	2.17	2	3640	55.973	59.212	75.754	-0.26	-0.22	0.74	0.78
GW02-(I)	151	447	852	40.2	23.4	0.42	17.6	0.83	3.4	3.5	3790	73.713	73.631	78.876	-0.07	-0.07	0.93	0.93
GW02-(II)	207	423	986	44.1	26.4	0.41	14.2	0.7	3.72	4.2	4510	83.520	83.392	93.861	-0.11	-0.11	0.89	0.89
GW02-(III)	157	449	639	39.9	20.5	0.37	19.1	0.3	3.87	4	3520	66.396	66.362	73.257	-0.09	-0.09	0.91	0.91
GW02-(IV)	180	460	576	46.4	28.1	0.32	12.1	0.56	3.49	3.6	3590	67.929	67.764	74.714	-0.09	-0.09	0.91	0.91
GW02-(V)-2	106	471	787	58.7	34.7	0.31	6.6	0.17	2.41	2	4370	71.978	78.087	90.947	-0.21	-0.14	0.79	0.86
GW02-(V)-3	106	453	774	58.2	28.8	0.3	6.5	0.17	2.3	2	4310	71.233	76.221	89.698	-0.21	-0.15	0.79	0.85
GW02-(VI)	108	444	1320	55.1	25.8	0.27	2.4	0.18	1.95	1.9	5640	96.244	97.613	117.378	-0.18	-0.17	0.82	0.83
GW02-(VII)	103	435	1290	54.7	22.5	0.24	1.9	0.21	1.83	1.6	6040	97.434	107.762	125.702	-0.22	-0.14	0.78	0.86
GW02-(VII)	102	448	1280	55.5	22.9	0.24	2	0.22	1.83	1.6	6040	97.671	107.999	125.702	-0.22	-0.14	0.78	0.86
GW03-B	0.01	489	77.5	62.9	446	6.46	97.1	0.05	7.38	7.2	3060	69.938	69.938	63.684	0.10	0.10	1.10	1.10
GW03-C-2	0.01	618	781	79.4	483	20.4	169	0.09	4.07	5.6	5170	98.756	98.672	107.596	-0.08	-0.08	0.92	0.92
GW03-E	0.01	475	278	61.9	294	14.4	108	0.07	3.52	6.5	3140	64.943	64.642	65.349	-0.01	-0.01	0.99	0.99
GW03-F	0.01	461	112	72.6	355	10.5	104	0.07	4.44	6.5	3140	63.018	62.982	65.349	-0.04	-0.04	0.96	0.96
GW03-G	0.01	441	565	82.9	377	14	153	0.08	4.11	4.2	3250	82.244	82.230	67.638	0.22	0.22	1.22	1.22
GW04-A	0.37	405	1530	67.4	152	17.4	55.6	0.16	3.73	5.3	4610	92.458	92.276	95.942	-0.04	-0.04	0.96	0.96
GW04-B	0.01	442	1160	64	214	18.3	52.5	0.1	4.07	6.5	3960	85.836	85.751	82.414	0.04	0.04	1.04	1.04
GW04-C	0.01	498	75.6	61.2	271	10.1	61.8	0.04	6.88	7	2440	54.470	54.470	50.780	0.07	0.07	1.07	1.07
GW04-D	0.01	503	152	65.1	244	6.78	64	0.06	6.12	6.8	2490	55.306	55.306	51.821	0.07	0.07	1.07	1.07
GW05-A	0.35	437	3980	80.4	215	12.7	36.5	0.24	3.42	5.8	10500	182.843	182.464	218.522	-0.16	-0.17	0.84	0.83
GW05-C-2	0.01	401	2280	66.5	215	17.4	47	0.23	3.58		6270	123.919		130.489	-0.05	-1.00	0.95	
GW05-D	0.5	392	3190	21.6	98.3	4.12	8.8	0.25	3.38	3.2	6290	143.339	143.553	130.905	0.09	0.10	1.09	1.10
GW05-F	0.01	443	1220	43.6	77.6	2.5	18.3	0.1	3.79	6	3730	74.299	74.139	77.627	-0.04	-0.04	0.96	0.96
GW05-H	0.01	429	1010	42.3	290	6.82	17.5	0.12	3.84	5.3	4180	83.641	83.502	86.993	-0.04	-0.04	0.96	0.96
SW-1-2	30.7	323	784	18.8	100	7.04	18.9	0.21	2.81	3.2	2870	58.916	57.998	59.729	-0.01	-0.03	0.99	0.97
SW-1-3	29.6	322	770	18.7	100	7.37	18.2	0.22	2.83	3.2	2930	58.152	57.304	60.978	-0.05	-0.06	0.95	0.94
SW-2-2	26.1	144	206	4.5	40.9	2.2	8.1	0.16	2.73	2.8	1420	23.233	22.956	29.553	-0.21	-0.22	0.79	0.78
SW-2-3	26.5	141	208	4.4	41.5	2.22	8.1	0.16	2.74	2.8	1320	23.205	22.970	27.471	-0.16	-0.16	0.84	0.84
														AVG	-0.09	-0.11	0.91	0.92
														STD DEV	0.11	0.18	0.11	0.10

The quality assurance program for the field program consisted of the following:

1. Establish field procedures a priori (using the previous sampling program on Lacnor as a basis);

2. Establish a field form for purposes of:

   - chain of custody,
   - recording observations, and
   - recording any alterations to previously established field procedures;

3. Inspection of field sampling professionals by additional person;

4. Flushing, cleaning of sampling tubes in piezometers; and

5. Cleaning of sample bottles.

The QA program for sample handling and shipment included the following components:

1. Sample handling using the field form as a chain of custody form; and
2. Sample shipment.

The QA program for laboratory components included:

1. Internal components; and
2. External components.

Internal components directed toward laboratory procedures, included the following:

1. The laboratories were forewarned of the program objectives.
2. An inspection and sample identification program was made by each laboratory.
3. Chain of custody documentation was in place.
4. The laboratories used control chart procedures.
5. Standard methods were used for doing analysis.
6. The laboratories used daily calibration procedures for the instruments.
7. The laboratories used internal standards on every 10-15 samples.

The following external laboratory components were used for the quality assurance program:

1. Submit one-half of the field samples for analysis. After obtaining satisfactory results from the first set of field samples, submit the last set of samples for analysis.

2. Duplicate approximately 20% of the samples, sending each sample to two check laboratories for quality assurance rather than to one.

3. Send replicate samples of each duplicate sample to each laboratory.

4. Submit prepared samples containing target concentrations of Th-230 to each laboratory in a chemical matrix ($FeSO_4$ and H_2SO_4) and pH similar to that of the natural water samples.

5. Check measurements of Th-232 made by radiochemical techniques with measurements of total thorium made by ICP (Indirectly Coupled Plasma).

The audit of laboratory performance was assessed using three methods:

a. agreement between laboratory,
b. accuracy of each laboratory, and
c. precision within each laboratory.

The agreement between laboratories measures relative bias. It was assessed using Youden Paired Sample Plots which are a plot of mean of Lab 1 vs. mean of Lab 2. The among lab standard deviation for each sample was used to define a 2 SD (Standard Deviation) Ellipse to identify lack of agreement.

The accuracy of each laboratory was measured relative to target values using synthetic samples. Youden Paired Sample Plots were used to define 2 SD Ellipses.

The precision within each laboratory was assessed using a duplicate-duplicate plot. This plot is a plot of high vs. low. It allows evaluation of change in precision as function of chemical concentration.

3.5.2 Data Quality Summary

A point form summary of the results of the external quality assurance program for the resampling of Th-230 in the Lacnor Tailings is given in Table 3.8. The results are divided into two sections in the Table: (i) agreement between laboratories and accuracy of each laboratory (Table 3.8a, entitled, "Analytical Bias - Paired Sample Plots) and (ii) Duplicate-Duplicate Plots (for assessing within-laboratory characteristics - i.e., the precision within each laboratory). Pertinent results from Table 3.8 and from other portions of the QA program are now described.

Evaluation of the duplicate sample results indicated reasonable analytical precision of approximately 6-7% relative standard deviations on Th-230 determinations within the activity range of the study. The absolute standard deviations typically increase with the activity of the sample. The three main participating laboratories were comparable with regard to the degree of precision achieved. Precision was approximately 10% relative standard deviations for natural Th and 15% for Th-232.

Activity concentration relationships of Th-230, Th-232 and natural Th suggest that SRC was underestimating Th-230 and overestimating Th-232. This was an obvious problem during the first sample submission, but was much less severe though still suggested by data during the second sample submission. During the first sample submission, Th-230 values reported by SRC were approximately one half those reported by other laboratories.

Youden paired-sample evaluations, summarized in Table 3.9, indicated a significantly high bias in the SRC Th-232 determination (outside the inter-laboratory 2SD limit in one sample pair during the first sample submission). A consistent tendancy toward Th-230 underestimation and Th-232 overestimation was observed, but was usually not statistically significant. The small number of laboratories involved limits the test sensitivity. During the second sample submission no significant bias was detected, indicating some improvement, though a consistent tendancy for overestimation of Th-232 by SRC was still suggested. There was no evidence of concurrent underestimation of Th-230 during the second sample submission.

TABLE 3.8A: SUMMARY OF RESULTS OF QUALITY ASSURANCE PROGRAM

TH-230

- o First Submission
  - Accuracy (Synthetic sample) - Reasonable (L2SD)
  - Field Bias (Natural sample) - SRC & ERI appear lower than MONENCO and BECQUEREL

- o Second Submission
  - Synthetic sample - Agreement
  - Natural sample - Agreement; No evidence of underestimation by SRC

TH-232

- o First Submission
  - Synthetic sample - Reasonable agreement
  - Natural sample - High bias by SRC

- o Second Submission
  - Synthetic sample - Good agreement
  - Natural sample - Slight, but no statistically significant over estimation by SRC

TH-228

- o First Submission
  - Synthetic sample - Reasonable agreement; MONENCO is 2 x SRC and BECQUEREL
  - Natural sample - Agreement

- o Second Submission
  - Synthetic sample - Agreement
  - Natural sample - Agreement

TABLE 3.8B: DUPLICATE-DUPLICATE SAMPLES

Duplicate-Duplicate Th-232

- o First Submission
  - BECQUEREL Slope = 1.0
  - SRC Slope = 1.2 - high bias - values double these of others
  - MONENCO Slope = 1.4
  - RSD is 15%

- o Second Submission
  - SRC more consistent than first set, but still high
  - RSD is 15%

Duplicate-Duplicate Th-230

- o First Submission
  - Precision good; RSD is 7%
  - Low bias by SRC at upper end - values half those of others

- o Second Submission
  - Precision good; RSD is 6%

Duplicate-Duplicate Th-228

- o First Submission
  - Good precision among 2 labs; RSD is 5%

- o Second Submission
  - Less precision than first submission; RSD is 15%

TABLE 3.9: SUMMARY OF YOUDEN PAIRED-SAMPLE PLOTS FOR EXAMINATION OF BIAS

Parameter	DATA OUTSIDE 2 SD RANGE		
	Low (-)	0	High (+)
First Submission			
Thorium	-	-	-
Th-230	-	-	-
Th-232	-	-	S
Th-228	-	-	-
Second Submission			
Thorium	-	-	-
Th-230	-	-	-
Th-232	-	-	-
Th-228	-	-	-

S = SRC

Anion-cation balances, based on laboratory ion determinations, were within 26% for all samples, and within 10% on average. The average charge deviations was negative, possibly due to the assumption that iron was in the reduced (+2) state. A substantial fraction of iron in the +3 state would balance the charge, and bring the majority of samples within acceptable (10%) limits.

3.5.3 Comparison to Previous Study Results

The previous sampling of the Lacnor Tailings Management area (Golder et al., 1986) involved chemical analysis for Th-230 and other radionuclides, cations, and anions upon approximately 55 porewater samples. The results of the quality assurance program from that study are given in Table 3.10. Six samples were analyzed under the QA program. A few samples demonstrate over an order of magnitude variation for Th-230.

The results of the QA program of this present study demonstrate differences between the laboratories and variations within the same laboratory. However, all three laboratories performed equally well in this present study and did not show the over order of magnitude variation noted in the previous study (Table 3.10). The main laboratory which made the porewater analyses previously (CHEMEX) no longer makes Thorium-230 measurements. The check laboratory in the previous study (MONENCO, whose samples are listed as "Duplicate" in Table 3.10) participated in the present study. Accordingly, it is not possible to project the QA performance from this present study to the QA results of the previous study.

Additional QA checks were made upon the two laboratories (CHEMEX, MONENCO) in the previous study (Golder et al., 1986) after the results indicated in Table 3.10 were reviewed. Samples with a defined value were submitted to the two laboratories, and the two laboratories obtained acceptable values (Golder et al., 1986). In addition, the two laboratories participated in other external QA programs developed by CANMET (Department of Energy, Mines and Resources) and obtained satisfactory results.

There are two resultant questions of concern:

1. Is the present data set a significantly better data set than the previous data set for purposes of establishing Th-230 levels in acidic tailings such as Lacnor?

TABLE 3.10: RESULTS OF GOLDERS et al. (1986) QA PROGRAM

Site	Piezo-meter	Tip Material	Depth (m)	Temp (°C)	DO (ppm)	pH	U (ppb)	Ra-226 (Bq/L)	Th-228 (Bq/L)	Th-230 (Bq/L)	Th-232 (Bq/L)
GW-01	b	R	11.84	7.0	0.80	4.9	5.9	1.65	0.08	1.84	0.08
GW-01	b	Duplicate					5.0	.39 ±.04	LT .005	.036 ±.012	.006
GW-02	I	T	7.90	8.0	0.95	5.0	9,800	15.00	0.66	13.00	0.66
GW-02	I	Duplicate					13,000	2.28 ±.13	N/A	1.68 ±.07	N/A
GW-05	a	ST	18.34	6.8	0.50	5.1	17.0	1.54	0.02	1.61	0.02
GW-05	a	Duplicate					19.5	.31 ±.04	N/A	.021 ±0.111	N/A
GW-07	t	R	8.14	5.2	0.60	7.2	3.7	0.04	0.05	0.10	0.05
GW-07	t	Duplicate					LT .5	.022 ±.011	LT .005	LT .005	LT .005
GW-03	f	T	4.62	6.5	0.45	6.05	110	4.76	0.03	1.00	0.03
GW-03	f	Duplicate					170	6.9 ±.3	.06 ±.01	.02 ±.01	LT .01
GW-05	e	T	9.24	7.0	0.6	5.95	60	4.55	0.09	1.32	0.09
GW-05	e	Duplicate					170	3 ±.2	.14 ±.01	.05 ±.01	LT .01

2. Can the previous data set be used with assurance for purposes of comparing changes over time; for purpose of establishing absolute values of Th-230 in Lacnor porewater in 1985, and for purposes of establishing Th-230 levels in other piezometers not sampled in this present study?

The present data set is a significantly better data set than the previous one due to the substantial resources devoted to the quality assurance program. The previous data set (Golder et al., 1986) can be used for the purposes listed above, but one is less certain of the quality of the data. A comparison of activity levels for samples from the same location measured in the two programs is another method for establishing one's confidence in the previous data. However, the levels are a strong function of pH (see Section 4). Accordingly, both the potential variations in laboratory performance demonstrated in this study, and geochemical variations over time (i.e., pH changes) must be considered for establishing one's confidence in the quality of the previous data set.

One final point is in order concerning the quality of the data set from the previous study. A most plausible explanation advanced by Golder et al. (1986) for the differences between the main laboratory and "check" laboratory was the precipitation of iron hydroxide in the sample bottle coprecipitating and removing Th-230 from solution. Each laboratory analyzed the liquid phase, rather than ensuring that any precipitate in the sample bottle was brought back into solution. One laboratory, after sample analysis, observed some precipitation in the bottom of a few sample bottles. This occurred due to insufficient addition of nitric acid as a preservative. This problem was avoided in the present study by ensuring that sufficient acid was added and by inspecting sample bottles. If this problem occurred on a random (unpredictable) basis in the previous study, it is not possible to establish with assurance which sample results in the previous study are suspect. Accordingly, it is concluded that the previous study results should be used with caution.

4.0 INTERPRETATION OF RESULTS

4.1 Qualitative Interpretation of Geochemical Control on Thorium-230

4.1.1 Origins of Thorium Isotopes

There are two major isotopes of thorium relevant to an understanding of Th-230 in the Lacnor Tailings: Th-232 (also called total thorium by mass) derived from the Th-232 decay chain, and Th-230, derived from the U-238 decay chain. Thorium-232 and daughters such as Th-228 are derived from thorium containing minerals in the ore. Thorium is rarely present in the ore as a pure mineral, but rather is associated with uranium minerals such as brannerite and contained as a substituent in lanthanium phosphate (monazite). After leaching and neutralization, thorium leached in the leaching pachucas reprecipitates probably as an amorphorus thorium hydroxide which ages to thorium oxide over time. Whether the uranium minerals are the only source of active thorium hydroxide/oxide in the tailings, or whether monazite makes a substantial contribution is a question which has not been satisfactorily answered. Its dissolution kinetics are sufficiently slow that it may not have a substantial impact in the mill with its 24 to 48 hour leaching times. However, in a tailings pile with substantial longer reaction times, it may dissolve significantly to release thorium in the tailings pile after milling.

Th-230 in the tailings pile is derived from leaching of U-238 containing minerals in the mill while Th-227 is derived from the uranium minerals containing U-235. The long half-life of Th-232 and Th-230 mean that their activity levels are defined by initial conditions. The short half-life of Th-228 means that its initial activity is a function of its own abundance in the ore. Subsequently its activity is a function of that of its parent Ra-228 and ultimately (over a decade of time), of the activity of the principal nuclide in the decay chain, Th-232.

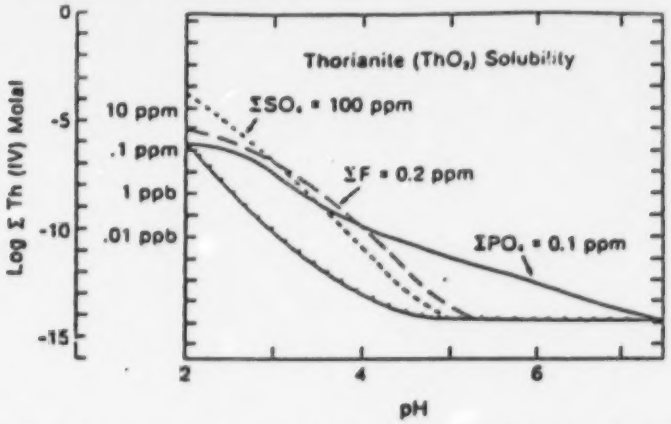
4.1.2 Qualitative Interpretation of Thorium Geochemistry

Solution Complexes

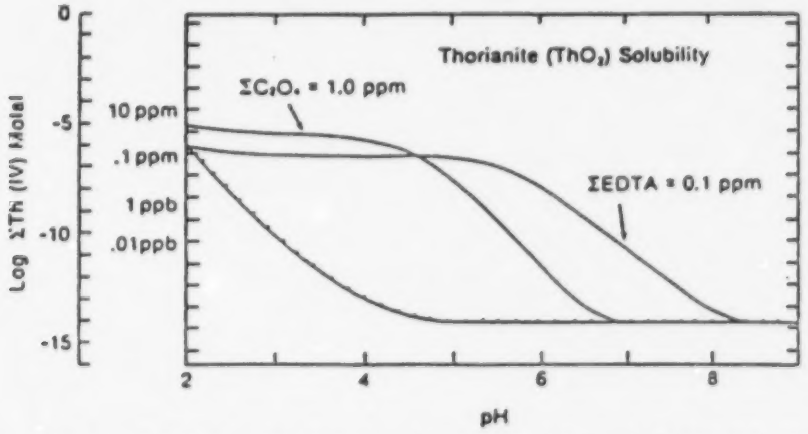
Thorium complexes with various anions, especially fluoride, hydroxide and sulphate.

FIGURE 4.1: THORIUM SOLUBILITY AS A FUNCTION OF pH

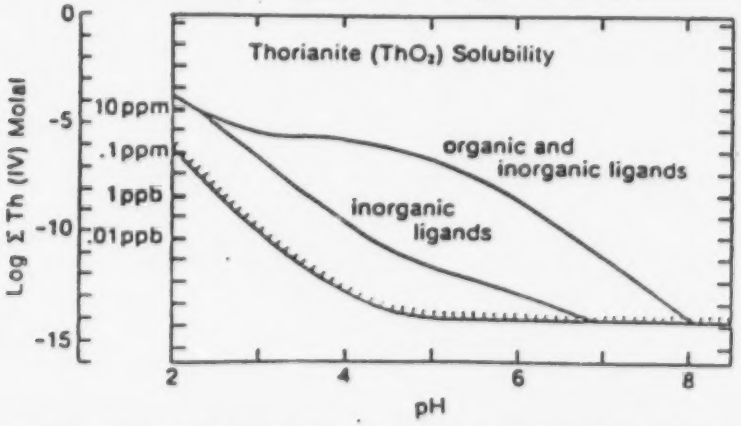
(from Langmuir and Herman, 1980)



The effect of thorium–sulfate, fluoride and phosphate complexing on the solubility of thorianite, $ThO_2(c)$, as a function of pH at 25°C. The cross-hatched curve denotes the solubility of thorianite in pure water. The curves indicating thorianite solubility as affected by complexing have been constructed assuming each ligand present in the absence of the others.



The effect of thorium-oxalate vs thorium–EDTA complexing on the solubility of thorianite, $ThO_2(c)$, as a function of pH at 25°C. The cross-hatched curve denotes the solubility of thorianite in pure water. The curves indicating thorianite solubility as affected by complexing have been constructed assuming each ligand present in the absence of the other.



The effect of thorium complexing on the solubility of thorianite. $ThO_2(c)$ vs pH at 25°C in a solution of ΣCl = 10 ppm, ΣNO_3 = 2.5 ppm, ΣSO_4 = 100 ppm, ΣF = 0.3 ppm, ΣPO_4 = 0.1 ppm, Σoxalate = 1 ppm, Σcitrate = 0.1 ppm and ΣEDTA = 0.1 ppm.

Sulphuric acid, because of its diabasic nature:

$$H_2SO_4 = H^+ + HSO_4^- \qquad K_1 = 10^3$$
$$HSO_4^- = H^+ + SO_4^{2-} \qquad K_2 = 1.26 \times 10^{-2}$$

will play a role in the chemistry of thorium. At high acid concentrations (pH 0-2), the bisulphate ion (HSO_4^-) is the main anionic species present, and the formation of the $Th(SO_4)_2$ complex is not possible. At low acid concentrations (greater than 2), the sulphate ion (SO_4^{2-}) becomes more predominant, therefore, the complex $Th(SO_4)_2$ will form. The stability of $Th(SO_4)_2$ decreases with increasing pH, leading to the formation of $Th(OH)_4(s)$.

Alternate Solid Phases

Th-230 will precipitate with $Th(OH)_4(s)$ or be coprecipitated after chemical neutralization in the mill. Plausible parent crystals for coprecipitation of Th-230 include gypsum, iron and aluminum hydroxide, and manganese dioxide. While coprecipitation phenomena are possible, the Th-230 data are interpreted in this report in terms of a solubility control by a thorium hydroxide solid phase. Because Th-232 has the largest mass of all thorium isotopes, its mineral phase - pore water behaviour will control the chemistry of Th-230. It will also control the chemistry of Th-228 initially (after deposition of the tailings from the mill). However, over the first decade, as Th-228 decays, the influence of Th-232 on Th-228 activity in the tailings may decrease to be replaced by the controls of Ra-228 chemistry. This will be found initially in Ra-228 containing minerals such as barite and anglesite but, over the long-term, the control of Th-228 will revert to Th-232 minerals due to ingrowth of Ra-228 from Th-232.

An analysis of available solubility constants for thorium hydroxide phases has been made. The data are given in Table 4.1. The aqueous concentration of thorium is plotted in Figure 4.1 as a function of pH for thorianite, the most insoluble phase of thorium (Langmuir and Herman, 1980). The plots indicate that thorium solubility is affected by organic complexes below pH 6.5. Assuming that the tailings do not have organics with substantial amounts of EDTA analogues, the solubility-controlled concentration of thorium will be relatively independent of pH above pH = 6. Similarly, phosphate levels of 0.1 ppm and higher (see table 3.2a) will affect the thorianite solubility below pH 8. Figures which give similar solubility curves as Figure 4.1 have not been made for the

TABLE 4.1: SOLUBILITY CONSTANT FOR THORIUM PHASE

Phase	Phase Name	Reaction Form	Solubility Constant	Reference
am-$Th(OH)_4$(s)	Amorphorus thorium hydroxide	-	?	-
$Th(OH)_4$(s)	not specifically given	Reaction 1 Reaction 2	log K = 9.4 log K = -46.6	Langmuir and Herman (1980) quoting Baes and Mesmer
-	Amorphorus thorium hydroxide	Reaction 1	log K = 6.3	SENES (1985)
ThO_2(act)	Active oxide	Reaction 3 Reaction 1	log K = -6.32 log K = 9.38	Baes and Mesmer (1976)
ThO_2(c)	Name not specifically given	Reaction 1 Reaction 2	log K = 6.3 log K = -49.7	Langmuir and Herman (1980) quoting Baes and Mesmer
ThO_2(c)	Well crystallized oxide	Reaction 3 Equation Rxn 1	log K = -9.6 log K = 6.3	Baes and Mesmer (1976)
ThO_2(th)	Thorianite	Reaction 1 Reaction 2	log K = 1.8 log K = -54.2	Langmuir and Herman (1980)
ThO_2	Completely insoluble (crystalline) thorium	Reaction 1	log K = 1.78	SENES (1985)

Notes:

1. Reaction 1: $ThO_2(s) + 4H^+ = Th^{4+} + 2H_2O$
   Reaction 2: $ThO_2(s) + 2H_2O = Th^{4+} + 4OH^-$
   Reaction 3: $ThO_2(s) + 2H_2O = Th(OH)_4(aq)$
2. Solubility Product Relationships:

   Rxn 1 (logK) = Rxn 2 (logK) + 56

   Rxn 3 (logK) = Rxn 1 (logK) - 15.9

other thorium phases. However, the conclusion that solubility is relatively independent of pH above pH = 8 appears appropriate for these phases.

The various solid phase data and the terminology used to describe them are summarized in Table 4.1. Combining the terminology of Baes and Mesmer (1976) and that of Langmuir and Herman (1980) results in three possible phases:

- o active oxide (terminology by Baes and Mesmer) which is the most soluble phase and presumed to be amorphorus thorium hydroxide (based upon Langmuir and Herman's terminology);
- o well-crystallized oxide (terminology by Baes and Mesmer); and
- o thorianite phase (terminology by Langmuir and Herman) which is least soluble.

Use of the terminology is somewhat different from that of SENES (1985) who label the "well-crystallized oxide" as "an amorphorus phase".

Langmuir and Herman (1980) note that the full range of log K values (7.6 log units separating the amorphorus and crystalline Th oxides and hydroxides) is "perfectly possible for a quadravalent cation such as Th^{4+}".

4.1.3 Qualitative Interpretation of Thorium Geochemistry

A qualitative interpretation of Th-230 geochemistry is aided by examining some of the data measured in this project. A summary of the data from the first sample submission is presented in Table 4.2 for the piezometer nest GW-2. The groundwater table is located approximately 1 m from the surface. In the depth zone of 2 to 4 m, the pH of the pore water is quite acidic (pH = 1.6-2) due to pyrite oxidation in the unsaturated zone. At these high pH's, levels of Th-232 (10-20 Bq/L) and Th-230 (150-200 Bq/L) are elevated due to the high solubility of thorium hydroxide at low pH's. However, deeper down in the tailings more removed from the downward transport of acidity, the pH is less acidic (pH 4-5). This causes lower levels of Th-232 (a range of detection limit to 0.1 Bq/L) and Th-230 (0.1-1 Bq/L) due to the lower solubility of thorium hydroxide.

A qualitative analysis of the Lacnor data suggests that pore water concentrations of Th-232 are approximately at equilibrium with a solid phase whose solubility constant is of

TABLE 4.2: RADIOISOTOPE MEASUREMENTS FOR PIEZOMETER NEST NO. 2 IN LACNOR TAILINGS AREA - FIRST SAMPLE SUBMISSION

	Ra-223	Th-227	Th-228	Th-230	Th-232	pH	Depth
GW-2-A		3.0 ±0.5*	0.22 ±0.07	0.12 ±0.05	0.02 ±0.02	5.4	16.1
GW-2-B-2	53 ±5	20.0 ±3.0**	0.65 ±0.30	0.32 ±0.18	LT 0.05	4.7	14.5
GW-2-B-3	58 ±6	20.0 ±30**	0.40 ±0.30	0.41 ±0.30	LT 0.05	4.7	14.5
GW-2-C		33.0 ±4.0**	1.5 ±0.8	2.2 ±0.9	0.21 ±0.10	3.9	10.4
GW-2-D			3.5 ±0.5	23.5 ±2.0	1.8 ±0.5	2.0	-
GW-2-i	44 ±5	14.0 ±2.0*	1.1 ±0.3	1.9 ±0.5	0.08 ±0.05	3.5	7.9
GW-2-ii	45 ±5	20.0 ±3.0*	1.0 ±0.2	1.8 ±0.5	0.14 ±0.07	4.2	-
GW-2-iii	45 ±5	16.0 ±2.0*	2.0 ±0.5	2.3 ±0.7	0.14 ±0.08	4.0	6.6
GW-2-iv	35 ±4	13.0 ±2.0	1.4 ±0.3	7.0 ±1.0	0.77 ±0.12	3.8	5.5
GW-2-V-2	26 ±3	11.5 ±2.5**	7.2 ±1.9	177 ±15	10.0 ±2.0	2.0	3.6
GW-2-V-3		9.5 ±2.0**	7.4 ±1.4	166 ±14	14.0 ±2.0	2.0	3.6
GW-2-Vi	22 ±3	11.5 ±2.5**	29 ±6	146 ±12	21.0 ±4.0	1.9	4.6
GW 02-(VII)-2			21.8 ±3.0	194 ±15	12.5 ±2.5	1.6	2.6
GW 02-(VII)-3			17.5 ±2.0	204 ±15	17.5 ±2.0	1.6	2.6

LT = less than

* As of February 19, 1988

** As of February 25, 1988

the order of log K = 6.3 (Reaction 1). But, because much of the thorium-232 in Lacnor tailings was originally in a monazite phase and uranium mineral, it is probable that the thorium phase present in the Lacnor tailings results from mill-induced (and/or acidic tailings-induced) dissolution of monazite and uranium oxide and its precipitation as crystalline ThO_2(c). However, the measured concentrations are for acidic solutions (pH ca 3). Hence, it is possible that a different phase may be stable at neutral pH.

4.1.4 Evaluation of Other Possible Solid Phases as Controllers on Th-230 in Porewater

An analysis was made of the possibility that Th-230 itself could form a solid phase which would control thorium-230 activity in the pore water. This possibility would occur for environments like Rabbit Lake where Th-232 has not been found in the pore water. For 2% UO_2 and complete dissolution of Th-230 into the pore water, the resultant pore water concentration is approximately 4×10^{-6}M. For the three phases, the solubility limit at neutral pH is approximately 5×10^{-7}M (8×10^{4} Bq/L) for the active oxide; 2×10^{-10}M (40 Bq/L) for the well-crystallized solid and 5×10^{-15}M (0.001 Bq/L) for the thorianite phase. Hence, it is possible that there is sufficient Th-230 present to form a thorium solid phase, by itself and in the absence of Th-232. This is doubtful, however, in the Elliot Lake situation where the ore rarely gets above 0.1% UO_2.

With respect to stable thorium, the global abundance of thorium in soils is 0.0005%, while the abundance in Cluff Lake ore is of the order of 0.0006%. Saskatchewan ores represent one plausible case for a Th-230 solid phase for motion due to their high UO_2 content and their low Th-232 content. Assuming that 10% of such soil type material is dissolved in the leaching pachucas results in approximately 2×10^{-9} mol Th-232/g dissolving. This is of a similar magnitude to Th-230 content of 2% UO_2 ore (1.5×10^{-9} mol Th-230/g solids), suggesting that both Th-230 and Th-232 could be involved in solid phase formation, irrespective of the source of the ore.

With respect to coprecipitation, it is plausible that Th-230 might coprecipitate with gypsum or barium sulphate. Barium sulphate is used as a precipitating solid for concentrating and purifying Th-230 for alpha spectrometry (e.g., Burk and Wiles, 1983) and also takes down other ions from solution (Mattioli and Wiles, 1985). In the case of potassium and Fe^{3+}, Mattioli and Wiles (1985) interpret their data to indicate that K coprecipitates with barium sulphate, but that Fe^{3+} either adsorbs or is occluded with the

solid phase. With respect to gypsum, one can, conceptually, describe the distribution of thorium-230 in gypsum by a relationship such as:

$$N_{ThCa} = D_{ThCa} \frac{(Th)}{(Ca^{2+})}$$

where: N_{ThCa} is the solid phase ratio of thorium in gypsum, and
D_{ThCa} is the distribution coefficient.
(Th) is the chemical activity of Th-232 plus Th-230

Observations upon Gunnar data indicate that the seepage water from the main tailings area form a precipitate after being allowed to stand for several hours. The precipitate removes most of the Th-230 from solution and is composed mainly of manganese and iron hydroxide. Whether the precipitate is amorphorus or crystalline is unclear.

Some further justification for this coprecipitation hypothesis could be sought by considering the ability of thorium (IV) hydroxide to coprecipitate with iron (III) hydroxide and manganese (IV) oxide. In this work, it is assumed that coprecipitation has a relatively minor role compared to that of Th-232 oxide. However, more work is required to definitively prove this assumption.

4.1.5 Summary

The solid phase levels of Thorium isotopes were measured previously by Golders et al. (1986). Their data indicate that Th-232 levels were typically of the order of 1 Bq/g and Th-230 typically 10 Bq/g. These ratios are similar to those observed in the porewater (see Table 4.2). At these levels, Th-232 constitutes over 99% of all thorium isotopes on a mass basis. Accordingly, it is concluded that Th-232 is the dominant isotope of thorium controlling the geochemistry of Th-230 and the two isotopes (Th-232, Th-230) should behave geochemically in a similar manner.

It is probable that the geochemical behaviour of Th-232 and Th-230 in Lacnor porewater is controlled by equilibrium solubility with secondary thorium hydroxide precipitates. Further mineralogical studies would be required to confirm this hypothesis.

When porewater is transported to surface waters, the geochemical controls upon Th-230 are not as well-defined. Based upon qualitative observations made previously (Golder et al., 1986) in which iron hydroxide precipitation is noted in groundwater seepage entering surface streams, it is probable that thorium isotopes are coprecipitated with the iron hydroxide. Quantitative evidence to confirm this point for the Lacnor tailings are not available. However, this interpretation is reasonable, and is used for assessing the potential dose of such waters to humans in the next section.

4.2 Qualitative Interpretation of Dosimetry Associated with Th-230 and Th-227

In the mathematical modelling of thorium uptake through various pathways to humans, the organic vs. organic speciation has been a vexing question. In this study, the following approach was used to estimate the radiological impact of thorium on humans.

The impacts of releases of U-238 decay chain radionuclides from tailings on man are measured in terms of ingestion and inhalation. In this study, ingestion is used. The annual dose that is calculated in this assessment is the annual effective dose equivalent based on stochastic (zero threshold) effects. Non-stochastic effects for doses received by individual organs are not considered, as it is unlikely that the threshold intake levels for non-stochastic effects would ever be approached by members of the critical group. The dose conversion factors used to equate annual radionuclide intake to dose are those given by Johnson and Dunford (1983).

There is some controversy concerning the dose conversion factors given by Johnson and Dunford (1983) for ingestion of thorium isotopes. For Th-230, two dose conversion factors are given, based on gut-to-blood fractional uptake factors (F_1) of 0.03 and 0.0002. The higher F_1 factor was intended to be applicable to thorium in organic form, such as in foods, while the lower factor was for inorganic forms, as expected to occur in drinking water. The higher dose conversion factor was under review in the recent past, since it appeared to calculate doses that are too high on the basis of thorium intake and dosimetry data. A downward revision of the higher dose conversion factor was made (J.R. Johnson, Chalk River Nuclear Laboratories, pers. comm.). The lower dose conversion factor for Th-230 is 1.4×10^{-7} Sv/Bq. This factor is nearly the same as the single dose conversion factor of 1.3×10^{-7} Sv/Bq recommended by ICRP (1979) for Th-230.

Drinking Water

The average annual dose received by an individual as a result of drinking water was modelled (BEAK, 1986) as:

$$d_{wi}(ing) = U_w \, L_w \, DCF_i(ing) \, C_{swi}$$

where: $d_{wi}(ing)$ = the average annual whole body dose due to the ingestion of radionuclide i in drinking water ($Sv \cdot a^{-1}$);

$DCF_i(ing)$ = the whole body dose conversion factor for the ingestion of radionuclide i ($Sv \cdot Bq^{-1}$);

U_w = the average annual intake of drinking water (0.6 $m^3 \cdot a^{-1}$);

C_{swi} = the calculated average annual concentration of radionuclide i in the drinking water source ($Bq \cdot m^{-3}$);

L_w = the fraction of the annual intake that is from the tailings pore water.

The fraction of the annual water consumption, that is from the tailings, was set equal to one. The annual water consumption is that defined for Reference Man by ICRP (1975).

Fish

The average annual dose received by an individual as a result of eating fish from a water similar to the tailings pore water was modelled as follows:

$$d_{fi}(ing) = DCF_i(ing) \, U_f \, C_f(t) \, L_f$$

where: $d_{fi}(ing)$ = the average annual whole body dose due to the ingestion of radionuclide i in fish ($Sv \cdot a^{-1}$);

$DCF_i(ing)$ = the whole <u>body dose</u> conversion factor for the ingestion of radionuclide i ($Sv \cdot Bq^{-1}$);

U_f = the average annual intake of fish (8E3 $g \cdot a^{-1}$);

C_{fi} = the <u>calculated</u> average annual concentration of radionuclide i in fish ($Bq \cdot g^{-1}$);

L_f = the fraction of the annual intake by fish that are grown in water similar to the tailings pore water.

The average intake of fish is based on the average consumption by male residents of Ontario (age 20 to 39) (Nutrition Canada, not dated).

Fish Contaminant Burden

A simple aggregate model was used to calculate the concentration of elements in the flesh of fish from water similar to the tailings. It is:

$$C_{fi} = B_{fi} C_{swi}$$

where: C_{fi} = the resulting annual average concentration of element i in fish tissue ($Bq \cdot g^{-1}$);

B_{fi} = water to fish transfer coefficient for element i ($Bq \cdot g^{-1}$ (wet weight) $\cdot$ $Bq^{-1} \cdot m^3$);

C_{swi} = the calculated average annual concentration of element i in lake water ($Bq \cdot m^{-3}$ or $ug \cdot m^{-3}$).

Data on bioconcentration factors for thorium are sparse. Many values are affected by water concentrations below detection limits. B_{fi} values can be calculated by using 0.5 of the less than values. When this procedure was done, for example, in western Canada application of UTAP, the resultant distribution was log-normally distributed. The geometric mean plus or minus three geometric standard deviations (expressed on a $\log_{10}$ scale) of the B_{fi} distribution for thorium from Western Canada brackets the value of 3.0×10^{-5} $m^3 \cdot g^{-1}$ recommended by Thompson et al. (1972) for thorium in freshwater fish.

Estimates of Risk

The critical point for making risk estimates is the activity of Thorium isotopes in the water phase. Direct consumption of Lacnor pore water is extremely unlikely due to the nature of the water of concern. The water is acidic and contains substantial amounts of iron. The ambient pH is at a point where thorianite or thorium hydroxide is elevated compared to solubility at more neutral pH conditions. Mixing of these pore waters with surface waters will result in more neutral conditions, and also cause dilution. Accordingly, the ambient concentration of surface waters will be less due to thorium hydroxide precipitation and due to dilution.

Two estimates of risk are given in this report. One is for the consumption of water similar in character to the bottom piezometer of GW-2 (pH = 5.4), and one for consumption of water similar in character to the upper groundwater zone of GW-2. The data for the bottom piezometer are used here to approximate the effect of dilution and partial neutralization in surface waters. The data for the upper piezometer are used to approximate conditions for a well water supply taken directly from the tailings. Risk estimates are not given for fish consumption because fish either could not live in water of such a low pH or they might survive but might not reproduce, or they would swim out of the zone if at all possible. Furthermore, it is highly unlikely humans would drink such water because iron precipitation may cause the water to be aesthetically unacceptable as drinking water, without treatment.

Results of the calculations are given in Table 4.2. The high values of Th-230 and Th-227 activity measured in the tailings pore water are used as a reference point. The DCF value used for Th-227 is 7.9E-8 Sv/Bq (Johnson and Dunford (1983). The calculations indicate that there is a small dose if surface water has characteristics of the deep piezometer. There is a potential dose of concern associated with the Th-230 activity levels if direct human consumption of the surface Lacnor pore water occurred. The dose estimates for Th-227 are much smaller than those for Th-230.

Further evaluation of the geochemistry of drinking water is recommended to refine these estimates. The evaluation could include (i) the probable pH and amount of dilution in surface water, (ii) the probable treatment of iron rich well water before consumption, and (iii) the change in Th-232 and Th-230 levels due to changes in pH controlled solubility.

TABLE 4.3: ESTIMATE OF RISK FROM TH-230 AND TH-227

Isotope	Surface Water Concentration (Bq/L)	RISK ESTIMATES FOR CONSUMPTION OF DILUTED LACNOR PORE WATER*		Porewater Activity (Bq/L)	RISK ESTIMATES FOR CONSUMPTION OF LACNOR PORE WATER	
		Water Consumption (uSv/a)	Fish Consumption (uSv/a)		Water Consumption (mSv/a)	Fish Consumption (mSv/a)
Th-230	0.1	0.8	0.4	170	1.4	-
Th-227	3	0.0007	0.00003	20	0.0045	-

*Assumes 1:1,000 effective dilution of pore water due to dilution and chemical precipitation effects

5.0 SUMMARY

A resampling of the Lacnor tailings management area was undertaken under a comprehensive quality assurance program to establish levels of Th-230 present in the pore water. This information is required because previous measurements varied with the laboratory. The data from this study can be used by the Atomic Energy Control Board and other agencies as background for assessing Th-230 in derived release limit calculations and in decommissioning submissions made by uranium mine and mill operations.

The quality assurance program involved field sampling, sample handling and transport, and laboratory and reporting components. The field sampling components involved establishing a set of prior protocols, field modifications as necessary, and their documentation on a sample collection sheet. Field work was carried out by experienced hydrogeologists; field work was inspected on-site by senior professionals to ensure that protocols were followed or modified as necessary, and by daily telephone contact. Sample bottles were leached and washed prior to sample collection; field blanks were taken. The sample collection sheet was used as the "chain-of-command" to trace both sample bottles from the time of sampling and the volumes sampled to the time of sample submittal.

The major QA activity for sample handling and transport was concerned with sample shipment to the participating laboratories because a company van was used to transport samples from the Lacnor tailings to Mississauga. Use was made of the original sample bottles in shipping samples to the prime laboratory. Aliquots were subsampled for submittal to the check laboratories.

The method of preparing check samples was different in this study than the conventional groundwater sampling program. The normal approach is a sequential set of samples from the same piezometer which are sent to the different laboratories. In this study, sequential samples were homogenized in one large clean container, prior to subsampling.

The laboratory quality assurance program involved internal and external components. The laboratories were forewarned about the objectives of the program. The laboratories used have all been audited previously under quality assurance programs. They follow

standard protocols, calibrate their instruments daily, and use internal standards on every tenth sample. The external QA program involved an assessment of within-laboratory variability precision by the submittal of replicates and between-laboratory variability using split samples. The same samples were used for both replicates and split samples. Both environmental samples and synthetic reference (known) samples were submitted. The synthetic samples were contained in a chemical matrix similar to that of the tailings pore water. For reporting, the original laboratory report is photographically reproduced in this report to avoid transcription errors.

The QA results indicate that the Th-230 measurements by the main laboratory (MONENCO) are not significantly different from the interlaboratory average on measurements of environmental samples and known synthetic samples within standard statistical limits. A similar conclusion is drawn with respect to their precision. In fact, the results from one check laboratory (SRC) suggested a significant underestimation of Th-230 on some environmental samples during the first submittal. This tendency was not significant during the second submittal.

A qualitative interpretation of the results suggest that the tailings pore water levels of Th-230 can be explained by its geochemical control by thorium hydroxide solubility, as opposed to coprecipitation phenomena.

The observed pore water concentrations of Th-230 represent a dose to a human being consuming such water of the order of 1 mSv/a. Assuming dilution and chemical precipitation of these porewaters occurred to reduce the activity by a factor of 1,000, the dose is approximately 1 uSv/a. The high dose levels associated with consumption of the porewater are unlikely because it is doubtful that human consumption of the water would occur before dilution and chemical precipitation substantialy reduce the Th-230 levels in surface waters. It is recommended that these dose estimates be refined by a quantitative geochemical interpretation of the Th-230 data along the groundwater gradient that such tailings pore water moves. Available field data are almost sufficient for such an evaluation. Some additional surface water samples may need to be collected to characterize thorium several hundreds of meters from the tailings pile.

Summary Statements

The following statements can be made from the results of this project.

1. Th-230 levels in Lacnor tailings range from approximately 200 Bq/L to less than detection limit. This range is mainly a function of the pH range and solubility effects. The pH range of less than 2 to greater than 5 is controlled by pyrite oxidation in the unsaturated zone and the downward transport of acidity.

2. The comprehensive quality assurance program used in this study gave a substantial improvement in confidence of the measurements, relative to the confidence in the quality assurance program used in the Golders et al., (1986) study on the same tailings.

3. Meticuluous care is required in all steps from the start of project initiation to procurement of final results.

4. The results of this project provides confidence in the ability of Canadian Laboratories to measure Th-230 levels. The analysis of duplicates by the three laboratories typically had a relative standard error of 15% or less.

5. The results of this project can be used to establish the number of inter-laboratory samples required as a function of the degree of confidence desired by the investigator.

6. The cost of the quality assurance program used in this project was larger than the cost of measuring all samples once. The results of this project show that subsequent sampling programs or routine programs should not need the same scope of a QA program. The following type of steps would aid in decreasing the cost of the QA program.

   (i) Define the program objectives before initiating the field program.

   (ii) Employ a tracking system for sampling, sample handling and shipment consistent with laboratory chain-of-custody procedures.

   (iii) After sampling, ensure that appropriate preservatives are used to keep the radionuclides in solution.

(iv) Submit samples for auditing the QA program by sub-dividing a well-mixed sample, rather than sequential samples from the same piezometer.

The QA program should include replicate samples submitted to each laboratory, particularly in the QA program, and an interlaboratory comparison which includes the replicate samples. Samples included in the QA program should also have high and low values. Where there is no previous information on Th-230 values, pH values may give some insight since Th-230 values may be elevated in acidic waters.

7. There are not a sufficient number of commercial laboratories in Canada to define an outlier laboratory for the measurement of Th-230 in an inter-laboratory comparison study. At least five to six laboratories are required to define an outlier laboratory; only three were available to this study.

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APPENDIX A

RESULTS OF GOLDERS ET AL. (1986) LACNOR STUDY

APPENDIX A.1

CHEMICAL RESULTS FOR CATIONS, ANIONS AND RADIONUCLIDES FROM PORE WATER OF LAC NOR TAILINGS

Table 1.10 - POREWATER - PHYSICAL, CHEMICAL AND RADIOLOGICAL ANALYSIS RESULTS FOR JUNE SAMPLES

POREWATER CHEMISTRY (JUNE READINGS)

SITE	PIEZO-METER	TIP MATERIAL	DEPTH (m)	TEMP (°C)	DO (ppm)	pH	E.C.@25 C (uS/cm)	Fe 2+ (ppm)	ACIDITY (ppm CaCO3)	Ag mg/L	Al mg/L	As ug/L	B mg/L	Ba mg/L	Be mg/L	Ca mg/L	Cd mg/L	Co mg/L	Cr mg/L	Cu mg/L	Fe mg/L
GW-01	a	ST-T	7.80	6.5	0.45	5.9	10000	4190	7000	<.05	5.2	4	<.04	<.05	<.005	453	<.1	<.5	1.7	.08	4740
GW-01	b	R	11.84	7.0	0.80	4.9	8400	3410	6100	<.05	13.9	6	<.04	<.05	<.005	481	<.1	.9	1.4	<.08	3830
GW-01	b	DUPLICATE								.04	13.3	20	1.45/1.33	.05	<.01	430	0.78	.77	.06	.045	3400
GW-01	e	T	2.57	6.5	0.80	<2.0	9400	890	1850	<.05	70.1	100	<.04	<.05	<.005	480	<.1	1.4	.5	<.08	958
GW-01	g	BLANK	-							<.005	.20	<1	<.004	.425	<.0005	.30	<.01	.14	.06	.019	.53
GW-01	h	BLANK	-							<.005	.20	<1	<.004	.364	<.0005	.24	<.01	.13	.02	.011	<.01
GW-02	a	ST	16.11	7.0	0.55	5.5	4970	1900	3340	<.05	1.7	6	<.04	<.05	<.005	453	<.1	<.5	.7	<.08	2040
GW-02	b	T	14.48	7.0	0.60	5.2	9010	4690	8800	<.05	35.8	4	<.04	<.05	.012	445	<.1	2.1	1.7	.17	4700
GW-02	c	T	10.36	7.0	0.70	5.75	4090	1620	3200	<.05	41.8	5	<.04	<.05	.021	485	<.1	4.7	.7	.18	1670
GW-02	e	T	1.02	12.0	1.25	<2.0	6800			<.05	16.5	110	<.04	<.05	<.005	559	<.1	.5	.2	.17	348
GW-02	i	T	7.90	8.0	0.95	5.0	5810	1790	6650	<.05	388	20	<.04	<.05	.075	451	<.1	4.0	.9	.10	1910
GW-02	i	DUPLICATE								.05	350	20	.82	.03	.08	410	.43	1.91	.21	.02	1760
GW-02	iii	T	6.60	6.0	0.60	4.15	4880	1340	3750	<.05	251	17	<.04	<.05	.011	473	<.1	2.0	.6	<.08	1420
GW-02	iv	T	5.51	6.0	0.65	3.95	5800	1620	4650	<.05	416	180	<.04	<.05	.009	454	<.1	2.6	3.8	<.08	1780
GW-02	v	T	3.58	6.0	1.20	1.75	13200	1285	2900	<.05	98.8	7	<.04	<.05	.005	459	<.1	2.4	.9	<.08	1410
GW-02	vi	T	4.60	6.5	1.70	2.3	9800	1560	4300	<.05	261	205	<.04	<.05	.009	454	<.1	2.5	3.4	<.08	1700
GW-02	vii	T	2.62	7.5	1.80	2.1	13200	1510	3200	<.05	98.7	80	<.04	<.05	<.005	474	<.1	2.3	.9	<.08	1640
GW-02	viii	T	1.48	9.0	0.90	<2.0	15000			<.05	54.3	800	<.04	.06	<.005	489	<.1	1.6	.5	.11	1210
GW-04	a	ST-T	11.89	6.5	0.50	5.8	9000	1340	1900	<.05	[illegible].5	3	<.04	<.05	<.005	460	<.1	1.2	.6	<.08	1350
GW-04	c	T	7.32	6.0	0.50	7.1	3700	55	2000	<.05	<.1	9	.64	<.05	<.005	538	<.1	.5	<.1	<.08	79.2
GW-04	e	T	4.14	5.5	0.50	6.7	3600	220	150	<.05	<.1	5	.77	<.05	<.005	530	<.1	<.5	.1	<.08	295
GW-04	f	T	2.82	6.0	0.50	6.4	4200	220	500	<.05	<.1	5	.64	<.05	<.005	508	<.1	<.5	<.1	<.08	222
GW-05	a	ST	18.34	6.8	0.50	5.1	7860	4860	8600	<.05	1.8	4	<.04	<.05	<.005	501	<.1	<.5	1.3	.09	5300
GW-05	a	DUPLICATE								.04	2.5	3	1.88/1.85	.03	<.01	460	1.04	.53	.06	.020	4800
GW-05	b	R	28.42	7.0	1.05	3.6	3400	220	500	<.005	<.01	<1	.095	.026	<.0005	122	.01	.17	.02	.010	22.1
GW-05	c	ST	22.10	6.5	0.55	5.4	8050	2850	4950	<.05	<.1	2	<.04	<.05	<.005	463	<.1	<.5	.8	<.08	3140
GW-05	d	T	10.90	6.5	0.40	3.8	7630	6255	10750	<.05	<.1	5	<.04	<.05	<.005	435	<.1	<.5	2.2	.11	6650
GW-05	e	T	9.24	6.8	0.40	3.55	8200	4635	8300	<.05	<.1	4	<.04	<.05	<.005	437	<.1	<.5	1.3	.10	5050
GW-05	f	T	7.95	6.5	0.42	5.7	8300	4020	7050	<.05	<.1	4	<.04	<.05	<.005	434	<.1	<.5	.9	.09	3940
GW-05	h	T	6.07	6.0	0.50	5.9	4000	1005	1750	<.05	<.1	4	<.04	<.05	<.005	480	<.1	<.5	.2	<.08	1070
GW-05	i	T	4.32	5.5	0.50	6.2	5400	1005	2200	.14	.5	4	<.04	<.05	<.005	443	<.1	<.5	.4	<.08	1270
GW-05	j	T	2.79	7.0	0.50	4.3	6400	280	1500	<.05	44.3	12	.15	<.05	.006	427	<.1	.9	.2	<.08	368
GW-05	k	T	1.12	10.8	0.60	4.8	2800	280	800	.12	2.2	90	<.04	.09	<.005	485	<.1	.7	.7	<.08	282
GW-05	l	POND	-	11.0	7.70	2.7	1800			<.005	10.0	2	.017	.079	.0007	114	<.01	.23	.05	.063	71.6
GW-06	b	R	13.47	6.0	0.60	6.65	210	30	100	<.005	.16	1	.069	2.21	<.0005	23.6	<.01	.06	<.01	<.008	3.46
GW-06	c	R	7.95	6.0	9.50	5.8	260														
GW-07	b	R	16.49	6.0	0.70	7.9	210	30	50	<.005	.15	1	.181	.764	<.0005	26.2	<.01	<.05	<.01	<.008	.08
GW-07	d	R	13.84	5.5	0.95	5.45	450	30	100	<.005	.07	2	.041	.136	<.0005	46.9	<.01	.17	<.01	<.008	12.3
GW-07	f	R	8.14	5.2	0.60	7.2	240	110	50	<.005	.07	7	.519	.970	<.0005	25.6	<.01	.07	<.01	<.008	<.01
GW-07	f	DUPLICATE								<.01	.09	15	.41	1.12	<.01	22	<.005	<.01	<.01	.005	.21
GW-08	a	LAKE	-	16.0		8.1	69	140	25	<.005	.09	<1	<.004	1.58	<.0005	9.40	<.01	.09	<.01	.009	<.01

Table 1.10 - POREWATER - PHYSICAL, CHEMICAL AND RADIOLOGICAL ANALYSIS RESULTS FOR JUNE SAMPLES - Page Two

SITE	PIEZO-METER	K (mg/L)	Mg (mg/L)	Mn (mg/L)	Mo (mg/L)	Na (mg/L)	Ni (mg/L)	P (mg/L)	Pb (mg/L)	Se (ug/L)	Si (mg/L)	Sr (mg/L)	Th (mg/L)	Ti (mg/L)	V (mg/L)	Zn (mg/L)	Zr (mg/L)	F^- (mg/L)	Cl^- (mg/L)
GW-01	a	140	171	16.4	<2	30	<.5	<5	<.05	<1	8.6	.90	1.0	.27	.31	1.9	.8	6.50	26.0
GW-01	b	110	203	24.2	3	40	<.5	<5	<.05	<1	7.4	1.14	<.5	.06	.27	2.8	<.5	3.20	27.0
GW-01	b	123	190	23	.28	56	.42	.28/.34	0.83	<1	16.3/16.6	.92	N/T	.34/.35	0.07	1.29	1.16	3.1	29.0
GW-01	e	58	33.1	.3	<2	<10	.7	<5	1.50	2	61.4	.45	1.5	2.95	.09	3.4	<.5	1.20	7.00
GW-01	g	2	.07	<.01	.2	1	<.05	<.5	<.05	1	.12	.017	.17	.010	.027	9.57	<.05	.01	1.59
GW-01	h	2	.02	<.01	.2	2	<.05	<.5	<.05	<1	.13	.009	.21	.007	.025	2.48	<.05	.02	1.53
GW-02	a	50	109	13.0	<2	10	<.5	<5	<.05	<1	8.1	.70	<.5	<.05	.18	1.7	<.5	2.40	8.00
GW-02	b	160	256	15.1	4	50	<.5	<5	<.05	<1	23.4	.84	4.4	2.97	.39	1.5	8.2	60.7	41.0
GW-02	c	60	103	2.5	5	<10	.9	<5	<.05	<1	20.1	.54	5.6	2.96	.30	7.1	7.6	57.1	8.00
GW-02	e	10	13.4	<.1	<2	<10	<.5	<5	1.65	5	57.0	.30	<.5	.30	.07	8.4	<.5	1.40	1.00
GW-02	I	60	75.2	.7	2	<10	1.6	<5	.35	<1	33.5	.53	2.8	.33	.60	8.4	.8	3.70	11.0
GW-02	I	61	71	.75	.02	16	1.69	.30	1.35	<1	76	.47	N/T	.38	.24	8.4	1.11	0.7	10.1
GW-02	III	50	69.9	.6	<2	<10	1.1	<5	.35	<1	36.6	.61	1.4	.11	.52	2.6	<.5	1.90	10.0
GW-02	Iv	70	62.8	.7	<2	<10	1.8	<5	<.05	<1	72.4	.38	2.3	.10	1.33	2.5	<.5	1.40	15.0
GW-02	v	60	42.4	.4	<2	20	1.1	<5	1.00	1	57.5	.36	10.2	5.15	.23	4.4	<.5	2.20	24.0
GW-02	vI	80	75.3	.6	<2	<10	1.1	<5	2.00	2	64.5	.52	12.1	1.94	.82	3.6	<.5	2.20	14.0
GW-02	vII	50	35.2	.4	<2	20	1.2	<5	.90	1	60.2	.33	8.1	5.47	.23	6.4	<.5	1.40	26.0
GW-02	vIII	30	23.4	.3	<2	<10	.7	<5	1.65	2	58.5	.31	1.4	5.04	.14	49.9	<.5	1.40	6.00
GW-04	a	60	187	21.8	<2	70	<.5	<5	<.05	<1	11.7	.96	.8	<.05	.29	2.4	<.5	1.20	49.0
GW-04	c	70	311	8.1	<2	70	<.5	<5	<.05	<1	6.7	.85	.7	<.05	.32	4.0	<.5	5.70	51.0
GW-04	e	70	259	21.1	<2	90	<.5	<5	<.05	<1	8.5	.82	<.5	<.05	.21	2.1	<.5	3.40	62.0
GW-04	f	70	341	10.5	<2	150	<.5	<5	<.05	<1	6.8	.69	<.5	<.05	.24	3.3	<.5	5.00	114
GW-05	a	90	258	13.7	<2	40	<.5	<5	<.05	<1	7.1	1.20	.6	.17	.31	2.1	.5	5.00	37.0
GW-05	a	104	250	12.8	.34	55	0.38	.23	1.05	<1	17.6	.87	N/T	.40	.09	.47	1.74/1.76	5.00	25.0
GW-05	b	6	23.3	1.27	.3	40	.06	<.5	<.05	<1	1.02	.282	.26	.005	.045	.39	<.05	.30	40.0
GW-05	c	70	238	19.9	<2	60	<.5	<5	<.05	<1	9.7	1.26	<.5	<.05	.28	1.7	<.5	1.20	41.0
GW-05	d	50	198	7.9	<2	10	<.5	<5	<.05	<1	13.2	1.37	<.5	<.05	.29	1.5	<.5	1.90	6.00
GW-05	e	20	145	4.8	<2	10	<.5	<5	<.05	<1	11.9	1.10	.6	<.05	.26	2.9	<.5	1.90	7.00
GW-05	f	40	96.5	3.7	<2	<10	<.5	<5	<.05	<1	11.0	1.21	.5	<.05	.19	2.3	<.5	1.90	10.0
GW-05	h	40	95.8	5.9	<2	20	<.5	<5	<.05	<1	8.4	.68	<.5	<.05	.12	3.6	<.5	3.30	21.0
GW-05	I	50	432	12.2	<2	20	<.5	<5	<.05	<1	9.9	.57	.9	<.05	.42	2.8	<.5	3.10	26.0
GW-05	J	20	1190	11.2	<2	10	.7	<5	1.50	<1	24.9	.70	1.2	.12	.85	2.3	<.5	5.50	25.0
GW-05	j	20	239	6.0	<2	10	5.3	<5	.80	<1	26.9	.44	.7	<.05	.32	28.2	<.5	3.10	16.0
GW-05	l	7	23.2	1.34	<.2	5	.12	<.5	<.05	<1	5.46	.114	.36	.028	.044	7.94	.06	.70	3.50
GW-06	b	6	8.43	.08	<.2	7	<.05	<.5	<.05	<1	4.80	.143	.10	<.005	.024	11.7	<.05	.26	5.40
GW-06	c																		
GW-07	b	6	9.09	.01	<.2	12	<.05	<.5	<.05	<1	4.37	.311	.10	.005	.026	10.2	<.05	.31	2.34
GW-07	d	9	16.1	1.79	<.2	11	.21	<.5	<.05	<1	8.63	.159	.13	<.005	.025	5.47	<.05	.30	3.00
GW-07	f	6	10.0	.05	<.2	14	<.05	<.5	<.05	<1	4.63	.206	.11	<.005	.019	4.93	<.05	.30	3.80
GW-07	f	9.5	9.7	.06	.01	12.4	.01	.12	<.01	<1	11.6	.18	N/T	.02	<.01	1.22	.03/.05	3.0	4.9
GW-08	a	2	1.62	<.01	<.2	3	<.05	<.5	<.05	<1	.52	.058	.14	.005	.026	5.33	<.05	.07	2.43

Table 1.10 - POREWATER - PHYSICAL, CHEMICAL AND RADIOLOGICAL ANALYSIS RESULTS FOR JUNE SAMPLES - Page Three

										POREWATER CHEMISTRY (JUNE READINGS)									
SITE	PIEZO-METER	PO_4^{3-} (mg/L)	NO^{3-} (mg/L)	NO^{2-} (mg/L)	B^{-} (mg/L)	SO_4^{2-} (mg/L)	$SO_4^{2-}(S_4)$ (mg/L)	$SO_4^{2-}(S_5)$ (mg/L)	NH_3-N (mg/L)	U (ppb)	Ra-226 (Bq/L)	Th-228 (Bq/L)	Th-230 (Bq/L)	Th-232 (Bq/L)	Ra-228 (Bq/L)	Pb-210 (Bq/L)	Pb-210 (Bq/L)	REDUCED S (mg/L)
Gw-01	a	<.1	<.05	<.02	<.1	8640	13400	8720	26.7	4.4	5.90	0.08	9.54	0.08				
Gw-01	b	<.1	<.05	<.02	<.1	7840	12100	8050	24.3	5.9	1.65	0.08	1.84	0.08				2000
Gw-01	b	<1	<.5	N/T	<.5	10900	N/T	N/T	20.2	5.0	.39+-.04	<.005	.036+-.012	.006				
Gw-01	e	<.1	<.05	<.02	<.1	4130	10200	4120	1.70	24.0	5.25	5.20	64.00	5.20				
Gw-01	g	<.1	<.05	<.02	<.1	.20	39.0	2.00	.20	1.1	0.03	0.12	0.20	0.12				
Gw-01	h	<.1	<.05	<.02	<.1	.10	18.0	1.80	.20	0.5	<0.01	0.15	<0.01	0.15				
Gw-02	a	<.1	<.05	<.02	<.1	4470	8980	4660	10.9	0.7	3.35	0.15	4.10	0.15	0.25	0.05	0.32	
Gw-02	b	<.1	<.05	<.02	<.1	9750	16200	9340	12.1	59.0	34.00	0.13	21.40	0.13	0.30	0.28	1.32	
Gw-02	c	<.1	<.05	<.02	<.1	3860	9520	4070	5.70	2800	38.20	0.08	18.10	0.08	0.60	0.30	2.76	
Gw-02	e	<.1	<.05	<.02	<.1	2850	8630	2810	1.60									
Gw-02	i	<.1	<.05	<.02	<.1	6650	12700	5840	3.60	9800	15.00	0.66	13.00	0.66	0.80	2.54	16.40	
Gw-02	i	<1	<.5	N/T	<.5	6000/6300	N/T	N/T	1.99	13000	2.28+-.13	N/A	1.68+-.07	N/A	2.8+-0.2	2.0+-.02	6.1+-0.3	1830
Gw-02	iii	<.1	<.05	<.02	<.1	4800	11200	4930	3.10	1980	17.40	0.45	9.70	0.45	0.60	3.82	21.90	
Gw-02	iv	<.1	<.05	<.02	<.1	6380	13400	5730	3.90	1020	18.60	3.40	2.80	3.40				
Gw-02	v	<.1	<.05	<.02	<.1	5510	13400	5570	2.60	15.0	8.30	40.90	330.00	40.90				
Gw-02	vi	<.1	<.05	<.02	<.1	6060	13600	6260	3.70	66.0	4.80	45.20	480.00	45.20	0.30	7.84	64.90	
Gw-02	vii	<.1	<.05	<.02	<.1	5290	13400	5410	3.60	4.4	3.50	33.10	315.00	33.10	0.30	3.38	37.50	
Gw-02	viii	<.1	<.05	<.02	<.1	5070			3.60									
Gw-04	a	<.1	<.05	<.02	<.1	4080	9910	3520	12.2	14.0	2.17	0.17	1.24	0.17				
Gw-04	c	<.1	<.05	<.02	<.1	2010	6890	2260	14.8	450	4.00	0.12	2.24	0.12				
Gw-04	e	<.1	<.05	<.02	<.1	2350	2550	2150	12.2	200	3.38	0.07	2.47	0.07				
Gw-04	f	<.1	<.05	<.02	<.1	2680	7890	2810	5.10	51.0	3.06	0.02	2.02	0.02	0.25	0.12	1.30	
Gw-05	a	<.1	<.05	<.02	<.1	9850	17000	9440	20.0	17.0	1.54	0.02	1.61	0.02				200
Gw-05	a	<1	<.5	N/T	<.5	10200	N/T	N/T	15.2/15.1	19.5	.31+-.04	N/A	.021+-.011	N/A				
Gw-05	b	<.1	<.05	<.02	<.1	363	11200	818	.30	3.3	0.25	0.05	0.18	0.05	0.25	<0.01	0.28	
Gw-05	c	<.1	<.05	<.02	<.1	6270	12600	6660	14.2	79.0	2.45	0.26	0.07	0.26				
Gw-05	d	<.1	<.05	<.02	<.1	10400	19600	12300	24.3	195	4.38	0.07	0.10	0.07				
Gw-05	e	<.1	<.05	<.02	<.1	8320	16800	9000	23.1	120	4.42	0.07	0.53	0.07				
Gw-05	f	<.1	<.05	<.02	<.1	6870	15400	7420	19.4	90	3.91	<.01	0.89	<.01				
Gw-05	h	<.1	<.05	<.02	<.1	3060	3430	2970	2.95	38.0	2.72	<.01	0.82	<.01				
Gw-05	i	<.1	<.05	<.02	<.1	4570	11400	4520	4.60									
Gw-05	j	<.1	<.05	<.02	<.1	5940	12800	5930	2.80									
Gw-05	k	<.1	<.05	<.02	<.1	2940	2290	2220	2.40	11.0	3.39	0.13	1.00	0.13				
Gw-05	l	<.1	<.05	<.02	<.1	671	17300	622	.50	92	1.45	0.75	7.23	0.75				
Gw-06	b	<.1	<.05	<.02	<.1	24.0	98.0	30.9	<.05	1.8	0.06	<.01	0.16	<.01				
Gw-06	c																	
Gw-07	b	<.1	<.05	<.02	<.1	6.90	98.0	10.4	<.05	1.5	0.06	0.07	0.07	0.07	<.05	0.03	0.72	
Gw-07	d	<.1	<.05	<.02	<.1	163	343	164	<.05	1.5	<.01	0.03	0.15	0.03				
Gw-07	f	<.1	<.05	<.02	<.1	39.7	213	43.2	<.05	3.7	0.04	0.05	0.10	0.05				57
Gw-07	f	<.1	<.02	N/T	<.05	46/49	N/T	N/T	0.13	<.5	.022+-.011	<.005	<.005	<.005				
Gw-08	a	<.1	<.05	<.02	<.1	20.4	20.0	19.9	<.05	4.0	0.04	0.05	0.12	0.05				

Table 1.11 - POREWATER - PHYSICAL, CHEMICAL AND RADIOLOGICAL ANALYSIS RESULTS FOR AUGUST SAMPLES

SITE	PIEZO-METER	TIP MATERIAL	DEPTH (m)	TEMP (°C)	DO (ppm)	pH	E.C. @25 C (uS/cm)	Fe 2+ (ppm)	ACIDITY (ppm CaCO3)	Ag (mg/L)	Al (mg/L)	As (ug/L)	B (mg/L)	Ba (mg/L)	Be (mg/L)	Ca (mg/L)	Cd (mg/L)	Co (mg/L)	Cr (mg/L)	Cu (mg/L)
GW-01	b	R	11.84	8.5	0.9	5.6	9000	12060	5960	<.005	<.01	2	.775	.024	<.0005	414	<.01	<.05	.01	.040
GW-01	f	T	1.24	13.5	1.2	2.1	5300	1340	1650	<.005	24.9	167	.044	.011	.0009	517	.01	.45	.02	.040
GW-02	a	ST	16.11			5.2	6000													
GW-02	b	T	14.48			5.0	10500													
GW-02	c	T	10.36	7.0	0.7	2.9	5300	5310	3000	<.005	52.2	2	.360	.011	.0315	436	.04	5.51	.24	.188
GW-02	d	T	2.60			<2.0	6400													
GW-02	e	T	1.02			<2.0	4200													
GW-02	I	T	7.90			3.6	6200													
GW-02	III	T	6.60	7.0	0.65	3.6	5700	5140	4500	<.005	323	19	.366	.010	.0143	412	.02	1.64	.14	.037
GW-02	Iv	T	5.51			3.4	5800													
GW-02	v	T	3.98	9.0	0.80	<2.0	14000	4580	5200	<.005	104	4	<.004	.006	.0040	437	.01	1.85	.25	.033
GW-02	vI	T	4.60			<2.0	11000													
GW-02	vII	T	2.62	11.5	1.3	<2.0	14000	4750	4950	<.005	100	125	<.004	.011	.0037	447	.01	1.70	.17	.056
GW-02	vIII	T	1.48			<2.0	12000													
GW-03	b	T	10.52	6.5	0.65	6.85	4500	391	250	<.005	<.01	5	.649	.018	<.0005	471	.01	<.05	.02	<.008
GW-03	d	T	7.67	6.5	0.5	6.60	5300	858	500	<.005	<.01	7	.565	.011	<.0005	472	<.01	<.05	<.01	<.008
GW-03	e	T	6.12	6.2	0.6	6.50	4200													
GW-03	f	T	4.62	6.5	0.45	6.05	4850	1620	1150	<.005	<.01	1	.708	.017	<.0005	442	.02	<.05	<.01	.010
GW-03	f	DUPLICATE								.02	.38	2/4	.89	.03	<.01	450	.075	.07	.04	.010
GW-03	g	T	3.05	9.0	1.0	6.20	5200	1560	1200	<.005	<.01	2	.695	.022	<.0005	442	.02	<.05	<.01	.014
GW-04	a	ST	11.89	6.5	0.65	5.0	9000	4410	2550	<.005	<.01	<1	.217	.052	<.0005	421	.03	.41	<.01	.027
GW-05	a	ST	18.34			5.80	9400													
GW-05	b	R	28.42			6.20	3300													
GW-05	c	ST	22.10	6.5	0.6	5.80	7650	9830	4850	<.005	<.01	<1	.240	.020	<.0005	413	.01	.15	<.01	.038
GW-05	d	T	10.90			5.95	12000													
GW-05	e	T	9.24	7.0	0.6	5.95	10000	15800	8900	<.005	<.01	1	.825	.016	<.0005	403	.03	<.05	<.01	.068
GW-05	e	DUPLICATE								.04	.34	3	1.43/1.4	<.01	<.01	340	.61	.16	.06	.020
GW-05	f	T	7.95	6.5	0.5	6.00	7400	11280	6100	<.005	<.01	2	.404	.019	<.0005	400	.04	<.05	<.01	.052
GW-05	h	T	6.07	7.2	0.6	6.20	4000	3300	1800	<.005	<.01	1	.304	.013	<.0005	454	.02	<.05	<.01	.021
GW-05	I	T	4.32	7.5	0.5	5.80	7400	4180	2100	<.005	<.01	2	.151	.010	<.0005	426	.02	<.05	.02	.021
GW-05	j	T	2.79			3.00	6000													

Table 1.11 - POREWATER - PHYSICAL, CHEMICAL AND RADIOLOGICAL ANALYSIS RESULTS FOR AUGUST SAMPLES - Page Two

SITE	PIEZO-METER	Fe (mg/L)	K (mg/L)	Mg (mg/L)	Mn (mg/L)	Mo (mg/L)	Na (mg/L)	Ni (mg/L)	P (mg/L)	Pb (mg/L)	Se (ug/L)	Si (mg/L)	Sr (mg/L)	Th (mg/L)	Ti (mg/L)	V (mg/L)	Zn (mg/L)	Zr (mg/L)
GW-01	b	3440	93	178	21.0	7.4	135	<.05	<.5	<.05	<1	5.63	1.36	<.05	.013	.126	.45	<.05
GW-01	f	345	8	15.2	1.17	.7	2	.48	.9	1.60	<1	61.9	.478	.34	.921	.043	.91	<.05
GW-02	a																	
GW-02	b																	
GW-02	c	1460	54	90.6	1.98	9.3	2	.73	<.5	<.05	<1	21.8	.497	5.90	2.40	.361	6.55	6.23
GW-02	d																	
GW-02	e																	
GW-02	I																	
GW-02	III	1380	55	61.0	.55	3.8	3	1.00	<.5	.40	<1	40.3	.548	.95	.109	.464	.70	.22
GW-02	Iv																	
GW-02	v	1370	59	32.4	.35	2.5	15	1.06	2.5	.95	2	68.0	.353	8.40	4.58	.198	.49	.11
GW-02	vI																	
GW-02	vII	1390	54	33.9	.33	3.0	14	1.27	3.3	.80	<1	72.9	.410	5.10	4.36	.170	6.30	.15
GW-02	vIII																	
GW-03	b	101	62	453	9.09	.4	99	.08	.6	<.05	<1	6.90	1.08	<.05	<.005	.207	1.16	<.05
GW-03	d	201	88	454	10.4	.5	208	<.05	<.5	<.05	<1	6.85	.943	<.05	<.005	.172	.62	<.05
GW-03	e																	
GW-03	f	307	83	379	11.5	.8	128	<.05	<.5	<.05	<1	7.05	.707	<.05	<.005	.209	.34	<.05
GW-03	f	340	76	420	13.3	.09	128	.04	0.1	0.36	<.5	12.8	0.82	N/T	0.25	0.03	0.42	.31/.30
GW-03	g	353	89	346	9.41	.8	181	.05	<.5	<.05	<1	7.61	.651	.11	<.005	.209	.45	<.05
GW-04	a	1360	63	175	20.0	3.2	82	.08	<.5	<.05	<1	11.6	.953	.15	<.005	.118	.24	<.05
GW-05	a																	
GW-05	b																	
GW-05	c	2700	71	222	18.0	4.7	54	<.05	<.5	<.05	<1	9.41	1.22	<.05	<.005	.158	.19	<.05
GW-05	d																	
GW-05	e	4370	16	132	4.29	10.7	8	<.05	<.5	<.05	<1	12.9	.976	.11	.008	.114	.57	<.05
GW-05	e	4100	24	130	4.0	.34	23	.09	.2/.2	1.23	<.5	25/23	0.88	N/T	.31/.34	0.09	0.47	1.41
GW-05	f	3030	37	79.4	3.13	6.7	7	<.05	<.5	<.05	<1	11.9	1.15	.13	.009	.102	1.33	<.05
GW-05	h	970	45	98.0	6.03	1.4	21	<.05	<.5	<.05	<1	9.11	.728	.09	<.005	.100	.58	<.05
GW-05	I	1150	42	385	12.6	1.9	18	<.05	<.5	<.05	<1	10.6	.583	<.05	<.005	.180	.62	<.05

Table 1.11 - POREWATER - PHYSICAL, CHEMICAL AND RADIOLOGICAL ANALYSIS RESULTS FOR AUGUST SAMPLES - Page Three

SITE	PIEZO-METER	F^- (mg/L)	Cl^- (mg/L)	PO_4^{3-} (mg/L)	NO_3^- (mg/L)	NO_2^- (mg/L)	Br^- (mg/L)	SO_4^{2-} (mg/L)	$SO_4^{2-}(S_4)$ (mg/L)	NH_3-N (mg/L)	U (ppb)	Ra-226 (Bq/L)	Th-228 (Bq/L)	Th-230 (Bq/L)	Th-232 (Bq/L)
GW-01	b	5.32	13.2	<1	<5	<.2	<.5	7960	8300	17.3	4.4	1.49	0.05	0.25	0.05
GW-01	f	1.83	3.50	<1	<5	<.2	<.5	2320	2450	1.00	108.0	2.71	0.86	5.26	0.86
GW-02	a														
GW-02	b														
GW-02	c	50.6	7.30	<1	<5	<.2	<.5	4230	4400	2.67	26500	24.30	0.09	15.20	0.09
GW-02	d														
GW-02	d														
GW-02	i														
GW-02	iii	<.05	7.50	<1	<5	<.2	.5	5270	5490	1.54	2900	14.50	0.54	7.40	0.54
GW-02	iv														
GW-02	v	<.05	21.2	<1	<5	<.2	.5	5530	5790	3.22	9.6	11.10	37.80	350.00	37.80
GW-02	vi														
GW-02	vii	<.05	19.2	<1	<5	<.2	.5	5440	5790	1.17	6.0	4.16	18.90	176.00	18.90
GW-02	viii														
GW-03	b	3.39	69.9	<1	<5	<.2	<.5	2880	2880	14.0	400	3.66	0.12	1.40	0.12
GW-03	d	4.23	172	<1	<5	<.2	<.5	3100	3100	11.7	660	4.58	0.05	1.15	0.05
GW-03	e														
GW-03	f	3.44	86.8	<1	<5	<.2	<.5	3400	3270	11.7	110	4.76	0.03	1.00	0.03
GW-03	f	1.9	95	<1	<.5	N/T	<.5	3400	N/T	13.3	170	6.9 +-.3	.06 +-.01	.02 +-.01	<.01
GW-03	g	3.24	117	<1	<5	<.2	<.5	3320	3360	3.81	26	5.10	0.05	1.84	0.05
GW-04	a	2.45	44.6	<1	<5	<.2	<.5	4270	4310	11.7	40	2.60	0.09	0.82	0.09
GW-05	a														
GW-05	b														
GW-05	c	4.59	34.3	<1	<5	<.2	1.0	6830	6700	13.0	60	2.49	0.13	0.13	0.13
GW-05	d														
GW-05	e	6.32	4.99	<1	<5	<.2	2.0	9210	9130	20.8	60	4.55	0.09	1.32	0.09
GW-05	e	1.9	8.4	<1	<1	N/T	<5	9000	N/T	21	170	3 +-.2	.14 +-.01	.05 +-.01	<.01
GW-05	f	4.59	1.59	<1	<5	<.2	2.0	6740	6870	13.3	54	4.29	.13	1.40	.13
GW-05	h	3.03	17.5	<1	<5	<.2	<.5	3100	3100	1.84	34	4.10	0.09	1.48	0.09
GW-05	i	3.60	19.5	<1	<5	<.2	<.5	4440	4310	2.22	72	3.67	0.06	1.15	0.06

APPENDIX A.2

FIELD SAMPLING PROCEDURES USED PREVIOUSLY BY GOLDER

FIELD SAMPLING PROCEDURES USED PREVIOUSLY BY GOLDER

Sampling Methodology

Prior to the collection of the porewater and groundwater samples, standing water was purged from the piezometers using a peristaltic pump and downhole tube to ensure that the water collected during sampling represented fresh water. It was possible to pump several of the piezometers dry. For these piezometers, the sample was collected on the same day as purging after there had been sufficient recharge of water to the piezometers. For the piezometers that could not be pumped dry using the peristaltic pump, three piezometer volumes of water were removed during the purging process.

Two methods were used to collect the water samples. For the samples for the measurement of field parameters and for the analyses of major cations, metals and anions, a downhole syringe sampler was used. The larger sample volumes for the radiological analyses were obtained using a peristaltic pump.

A typical syringe sampler consists of a modified 50 mL plastic syringe (Feenstra et al., 1985). The syringe sampler was fitted with a plastic 25 mm filter holder and 0.45 um filter membrane. The sampler was connected to a dedicated length of polyethylene tubing using a one-holed rubber stopper and was lowered down the piezometer to the level of the piezometer intake. A vacuum pump was used to actuate the syringe plunger and draw water through the filter into the syringe. The syringe sampler was then removed from the piezometer and immediately capped with a sleeve serum stopper to prevent exposure of the sample to the atmosphere. Preservatives, if required, were added directly through the serum stopper using a 1 mL plastic syringe.

The modification of the sample syringe included the cutting of the plastic plunger just above the tip, and the trimming of the wings so that the syringe could fit down the piezometer. These modified syringes were washed with a 10 percent solution of hydrochloric acid and rinsed several times with distilled water. The syringes were then individually wrapped in plastic bags and stored for use in the field.

For the radiological samples, the peristaltic pump was connected directly to a downhole length of polyethylene tubing. Each piezometer that was sampled had a dedicated length

of polyethylene tubing to minimize the potential for cross-contamination between piezometers. A 142 mm filter holder with 0.45 um filter membrane was connected to the pump discharge to filter samples.

The various parameters to be analyzed required that different sampling and handling procedures be used. These procedures are outlined below.

i) Electrical conductance and pH were measured using a combination pH and conductance meter (Myron L pDS Meter, Model EP-10/pH). The instrument was calibrated at the beginning of each day using pH 7 and pH 4 buffer. Between each reading, the accuracy of the instrument was checked using the pH 7 buffer.

The measurement was made using a 50 mL unfiltered aliquot which was collected using a syringe sampler. The first 30 mL of the aliquot which was used to rinse the sample chamber of the instrument. The final 20 mL was used for the sample analysis. This meter internally calibrated the conductivity readings to 25°C.

For the June sampling, the pH and conductance in 13 piezometers at monitoring sites GW-02 and GW-05 (a and b), were measured using the Corning combination Meter 610A and the YSI Model 33 Temperature, Conductivity and Salinity Meter, respectively. For these readings, water was pumped to the surface using a peristaltic pump. As with the Myron meter, the Corning meter was calibrated using the two buffers at the beginning of each day and checked between sample measurements with the pH 7 buffer. Electrical conductance readings were standardized to 25°C.

The use of the Corning and YSI meters was discontinued after 13 of the sample measurements in June because of electrical problems in internal components of the Corning meter. Subsequently the Myron meter was used for both pH and conductivity measurements.

ii) Eh was to be measured using the Corning Meter 610A with an Eh electrode. However, problems were encountered in the field during June with calibration of the meter and electrode, unstable readings, and electrical failure of the meter. Because of the above, Eh measurements were discontinued during June and were

not made in August; however, Eh conditions can be estimated using relationships between ferrous and ferric iron concentrations if it is assumed that the ferric iron concentration represents the difference between those for total and ferrous iron.

iii) Ferrous iron and acidity were measured by titration in the CAIRS office laboratory. The procedures used for the titrations are presented in Appendix 5.

Samples were collected using the syringe samplers and stored under refrigerated conditions until titrations were performed. Two 50 mL syringes from each piezometer were delivered to the CAIRS field laboratory, where one member of the sampling crew performed the analyses immediately following delivery. To facilitate sampling efficiency, samples from several piezometers were collected prior to each trip to the laboratory. Generally, three sets of samples were delivered to the laboratory each day.

iv) A 50 mL syringe sample was collected for anion analyses (IC scan). This sample was filtered down-hole and kept refrigerated until the sample was delivered to the appropriate analytical laboratory.

v) A 50 mL syringe sample was collected for the analyses of major cations and metals. This sample was filtered down-hole, preserved with about 0.2 mL of concentrated HNO_3, and kept refrigerated until sample delivery to the analytical laboratory.

vi) Two 50 mL syringe samples were collected for the analysis of dissolved reduced sulphur. Both syringes were filtered down-hole. One of the syringes was preserved with about 0.1 mL of 50 percent HCl and the other with about the same amount of 5 percent H_2O_2. The samples were refrigerated until they were delivered to the analytical laboratory.

For the June sampling, problems were encountered with the analyses of reduced sulphur. Due to the very high concentrations of sulphate and the low concentrations of reduced sulphur species, the determination of reduced sulphur as the difference between the concentrations of the total sulphur and sulphate was unreliable.

viii) Two litres of sample were collected in two plastic sample bottles for radionuclide analysis. The samples were collected using the peristaltic pump, filtered in the field, and acidified with about 2 mL of concentrated HNO_3 for preservation.

ix) Temperature and dissolved oxygen were measured down-hole using a YSI Model 57 Temperature and Dissolved Oxygen Meter. Measurements were made after the other water samples had been collected. This ensured that contaminants from other piezometers were not introduced to a piezometer by the downhole probe prior to the collection of water samples for chemical analysis.

APPENDIX A.3

FIELD SAMPLE SHEET USED IN THIS STUDY

ATTACHMENT 4 **FIELD SHEETS**

Date: _____

1. Piezometer/Sample Number _____ Piezometer Description (diam., type) _____

2. Condition of Piezometer _____

3. Depth to Water:Before Sampling _____
   Depth to Water:After Sampling _____

4. Flushing

   - Date, time _____ Volume Removed _____
   - Characteristics of Water _____

5. Sample Bottles Collected:

Identifying Number	Sample Container	Sample Volume	Filtered	Type and Volume of Preservative
1	_____	_____	Y/N	_____
2	_____	_____	Y/N	_____
3	_____	_____	Y/N	_____
4	_____	_____	Y/N	_____
5	_____	_____	Y/N	_____

Storage: _____

Remarks: _____

_____

6. Field Measurements: Temp. _____
   Sp. Cond. _____
   pH _____

7. Sampled by: _____

8. Comments: (i.e., variance from procedure, field condition, wind speed, etc.): _____

_____

_____

_____

9. Sample Transmittal Procedure:

To:	_____	_____
By:	_____	_____
Date/Time:	_____	_____

APPENDIX B

ANALYTICAL METHODS USED BY VARIOUS LABORATORIES

APPENDIX B.1

ELEMENTAL RESEARCH INC.
ICP-MS PROCEDURES AND RESULTS

ERI Ref : 151-40-03

The following are the results of our examination o your samples for the presence of Thorium isotopes.

	^{228}Th	^{230}Th	^{232}Th
Sample			
GW02-B-2	<0.005	<0.005	1.32
• GW02-(v)-2	<0.005	0.18	8,600 •
SW01-3	<0.005	0.009	123

Values given are in micrograms per litre.

• This sample diluted X100. Undiluted sample grossl saturated the detector.

ANALYSIS PROCEDURE

Standardization

The following standards were employed in the analysis.

2% Nitric Acid Blank
0.1ppb Thorium 232 in 2% Nitric Acid
1ppb Thorium 232 in 2% Nitric Acid
10ppb Thorium 232 in 2% Nitric Acid
100ppb Thorium 232 in 2% Nitric Acid

Analysis Procedure

1. The mass spectrometer was tuned up to give maximum (peak) countrate on ^{232}Thorium.
2. The span of the mass range was set to cover 227 daltons through 234 daltons.
3. Scan parameters were established to give a total acquisition time of two minutes for 480 scans.

Duplicates

The samples were analysed in duplicate.

Sample GW02-(v)-2 was analysed as received, diluted X10 and X100. Gross detector saturation occurred on run 1, with the same on run 2 (X10 dilution) for ^{232}Th.

Sample	^{232}Th Replicates (µg/l)	•Mean•
GW02-B-2	1.19	
	1.44	•1.32•
GW02-(v)-2	8,444	
	8,800	•8,622•
SW01-3	138	
	108	•123•

Limits of Detection

The Detection Limit is determined as twice the background value.

APPENDIX B.2

ANALYTICAL METHODS USED BY BARRINGER

ANALYTICAL METHODS USED:

Metals (exc. Pb)	- Inductively-Coupled Argon Plasma Emission Spectroscopy (ICAP) - ARL Model QA-137 - Refs.* - SM: 305 - MOE: MD54 - EPA: 200.7
Pb	- Flame Atomic Absorption - Varian Model AA-V - Refs.* - SM: 303A - MOE: MD21 - EPA: 239.1
Conductance	- Meter with Flow-Through Cell - Radiometer CDM83 - Refs.* - SM: 205 - MOE: CI1 - EPA: 120.1
Anions	- Ion Chromatography - Dionex 2110i - Refs.* - SM: 429 - MOE: CD18, NB1, SH12 - EPA: 300.0

NOTE: 1. Anion Analyses - required 100-fold dilution
- if a more concentrated solution was tried precipitation occured
- as a result, the detection limits were degraded accordingly

*REFERENCES:

SM : APHA-AWWA-WPCF, Standard Methods for the Examination of Water and Wastewater, (16th edition) 1985

MOE : Ontario Ministry of the Environment, Handbook of Analytical Methods for Environmental Samples - 1983

EPA : U.S. Environmental Protection Agency, Methods for the Analysis of Waters and Wastes - 1983

APPENDIX B.3

SRC QUALITY CONTROL MEASURES AND ANALYTICAL PROCEDURES

Saskatchewan
Research Council 30 Campus Drive Saskatoon, Sask. Canada S7N 0X1 Phone: (306) 664-5400 Telex: SARECO 074-2484

SRC Analytical Laboratory

Quality Control

The laboratory participates in more than 10 inter-laboratory quality assurance programs within Canada and the United States. Most of these are repeated 2 to 4 times yearly. These programs encompass trace metal measurements on water and solids, major water constituents and radiochemical determinations on liquids, solids and filters. All methodology is checked for recovery, precision and accuracy by analyzing NBS, CANMET and similar reference standards. The laboratory has routinely participated in the standardization of reference materials (primarily in the radiochemical field). In addition to the foregoing, blind duplicates, spiked samples and blanks are routinely processed with each group of samples analyzed. These internal quality control checks constitute approximately 10% of the analytical workload. All radiochemical procedures are calibrated and checked with NBS traceable standards (some directly from NBS and others from Amersham).

SASKATCHEWAN RESEARCH COUNCIL ANALYTICAL SERVICES

Total Thorium

Thorium is isolated from prepared sample solutions by coprecipitation first with lanthanum hydroxide, then lanthanum fluoride, followed by extraction with thenoyltrifluoroacetone (TTA) in a suitable solvent. The organic extract is stripped with a nitric acid solution to produce an aqueous solution of thorium. The colour development is performed by reacting a strong HCl solution (approximately 6 N) of the isolated thorium with an aqueous solution of arsenazo III. The colorimetric measurement is then performed at a wavelength of 665 nm.

Reference Standard:

Amersham aged thorium nitrate

Detection Limit = 0.1 ug/L

Precision = <0.5 ug ± 10%
>0.5 ug ± 3%

SASKATCHEWAN RESEARCH COUNCIL ANALYTICAL SERVICES

Thorium-230

Tracer: Thorium-234

Sample decomposition: Potassium pyrosulphate fusion

Thorium is separated from prepared sample solutions by coprecipitation with barium sulphate. Barium sulphate is dissolved in a strongly alkaline solution of ethylenediaminetetraacidic acid. Thorium is precipitated as hydroxide with 50 µm cerium carrier. The precipitate is mounted on a 25 mm 0.2 micron membrane filter for alpha spectrometry. Alpha spectrometry is performed using a vacuum chamber mounted surface barrier detector.

Reference Standard:

Std#1 Amersham aged thorium nitrate

Std#2 Alfa Chemicals thorium oxide 99.9%

It was assumed that Th-230 would give the same response as Th-232 and Th-228 from these standards (i.e. cpm/pCi).

Detection Limit = 0.01 Bq

Precision = 0.18 - 0.37 Bq ± 10%

>0.37 Bq ± 5%

APPENDIX C

COMPILATION OF TABLES AND FIGURES

APPENDIX C.1

TABLE 3.2a ANALYTICAL RESULTS FOR ANIONS AND CATIONS (MEASURED BY BARRINGER)

TABLE 3.2a: ANALYTICAL RESULTS FOR ANIONS AND CATIONS (measured by Barringer)

SAMPLE ID	AG MG/L	AL MG/L	B MG/L	BA MG/L	BE MG/L	CA MG/L	CD MG/L	CO MG/L	CR MG/L	CU MG/L
GW01-A	<.005	3.53	<.004	.019	.0043	376	<.01	.45	<.01	.049
GW01-B-2	<.005	2.10	<.004	.037	.0033	391	.01	.47	<.01	.050
GW01-B-3	<.005	2.16	<.004	.038	.0033	405	.02	.53	<.01	.051
GW01-C	<.005	13.9	<.004	.016	.0063	417	.02	.53	<.01	.045
GW01-D	<.005	163	<.004	.022	.0079	433	<.01	1.29	.61	.028
GW01-E	<.005	83.8	<.004	.012	.0042	462	<.01	1.04	.01	.154
GW02-A	<.005	1.38	<.004	.023	.0036	417	<.01	.34	<.01	.026
GW02-B-2	<.005	25.5	<.004	.020	.0261	387	.02	.86	<.01	.053
GW02-B-3	<.005	24.6	<.004	.019	.0258	386	.02	.82	<.01	.051
GW02-C	.017	78.1	<.004	.008	.0242	448	<.01	1.22	<.01	.032
GW02-D	<.005	50.7	<.004	.015	.0024	430	<.01	.65	<.01	.141
GW02-(I)	.010	151	<.004	.011	.0150	447	<.01	1.06	<.01	.035
GW02-(II)	.008	207	<.004	.010	.0143	423	<.01	1.23	.04	.024
GW02-(III)	.007	157	<.004	.009	.0079	449	<.01	.71	.02	.019
GW02-(IV)	.014	180	<.004	.011	.0071	460	<.01	.65	1.03	.017
GW02-(V)-2	<.005	106	<.004	.007	.0059	471	<.01	.99	.43	.023
GW02-(V)-3	.007	106	<.004	.008	.0057	453	<.01	.97	.43	.023
GW02-(VI)	<.005	108	<.004	.014	.0054	444	<.01	1.65	.13	.024
GW02-(VII)-2	<.005	103	<.004	.015	.0052	435	<.01	1.60	.01	.023
GW02-(VII)-3	<.005	102	<.004	.015	.0055	448	<.01	1.60	.05	.024
GW03-B	.018	<.01	.567	.014	.0025	489	<.01	.10	.09	.019
GW03-C-2	.007	<.01	.206	.011	.0025	418	<.01	.11	<.01	.019
GW03-E	.014	<.01	.579	.014	.0026	475	<.01	.07	.03	.017
GW03-F	.017	<.01	.760	.014	.0026	461	<.01	.07	.08	.020
GW03-G	.014	<.01	.570	.011	.0025	441	<.01	.09	<.01	.016
GW04-A	<.005	.37	<.004	.021	.0034	405	.01	.82	<.01	.026
GW04-B	<.005	<.01	<.004	.014	.0026	442	<.01	.15	<.01	.019
GW04-C	.012	<.01	.637	.014	.0022	498	<.01	.06	.07	<.008
GW04-D	.016	<.01	.520	.013	.0024	503	<.01	.06	.06	.009
GW05-A	<.005	.35	<.004	.022	.0038	437	.02	.73	<.01	.058
GW05-C-2	<.005	<.01	<.004	.018	.0028	401	<.01	.78	<.01	.032
GW05-D	<.005	.50	<.004	.012	.0030	392	.02	.34	<.01	.044
GW05-F	<.005	<.01	<.004	.011	.0022	443	<.01	.13	<.01	.024
GW05-H	<.005	<.01	.007	.013	.0027	429	<.01	.13	<.01	.027
SW-1-2	<.005	30.7	<.004	.014	.0040	323	<.01	.37	<.01	.105
SW-1-3	.006	29.6	<.004	.014	.0042	322	<.01	.37	<.01	.104
SW-2-2	<.005	26.1	.042	.014	.0027	144	<.01	.28	.05	.229
SW-2-3	.010	26.5	.040	.014	.0027	141	<.01	.27	.05	.226
CONTROL DATA	--	--	--	--	--	--	--	--	--	--
DET. LIMS.	.005	.01	.004	.005	.0005	.01	.01	.05	.01	.008
BLANK	.005	.01	<.004	<.005	<.0005	.04	<.01	<.05	<.01	<.008
BLANK	<.005	<.01	<.004	<.005	<.0005	.08	<.01	<.05	<.01	<.008
GW02-C	.017	78.1	<.004	.008	.0242	448	<.01	1.22	<.01	.032
GW02-C-R	.028	80.3	<.004	.008	.0240	459	<.01	1.21	<.01	.033
SW-2-2	<.005	26.1	.042	.014	.0027	144	<.01	.28	.05	.229

TABLE 3.2a: ANALYTICAL RESULTS FOR ANIONS AND CATIONS (measured by Barringer) (cont'd)

SAMPLE ID	AG MG/L	AL MG/L	B MG/L	BA MG/L	BE MG/L	CA MG/L	CD MG/L	CO MG/L	CR MG/L	CU MG/L
SW-2-2-R	<.005	26.4	.053	.014	.0027	150	<.01	.27	.06	.234
GW04-C	--	--	--	--	--	--	--	--	--	--
GW04-C-R	--	--	--	--	--	--	--	--	--	--
CONTROL STD	<.005	.92	.207	1.00	.0190	<.01	.20	.16	.19	.202
CONTROL.EST.	--	1.00	.200	--	.0200	--	.20	.20	.20	.200
EPA STD	<.005	.12	.099	<.005	<.0005	40.4	<.01	<.05	<.01	.015
EPA.STD(CRT)	--	--	--	--	--	40.0	--	--	--	--

TABLE 3.2a: ANALYTICAL RESULTS FOR ANIONS AND CATIONS (measured by Barringer) (cont'd)

SAMPLE ID	FE MG/L	K MG/L	MG MG/L	MN MG/L	MO MG/L	NA MG/L	NI MG/L	P MG/L	PB MG/L	SI MG/L
GW01-A	2900	88.6	162	15.5	.7	27.4	<.05	<.5	<.05	10.1
GW01-B-2	3160	106	158	17.4	<.2	25.6	<.05	.7	<.05	8.45
GW01-B-3	3200	108	164	17.5	<.2	25.9	<.05	.7	<.05	8.44
GW01-C	2650	92.0	148	13.9	<.2	18.2	<.05	.7	<.05	20.1
GW01-D	1160	82.9	65.0	.67	<.2	3.4	.52	1.5	<.05	37.2
GW01-E	792	43.2	15.7	.26	<.2	1.5	.30	2.4	1.90	41.0
GW02-A	1690	56.4	111	11.9	<.2	10.3	<.05	<.5	<.05	9.28
GW02-B-2	3100	118	181	17.4	.6	38.0	<.05	.6	<.05	13.1
GW02-B-3	3080	117	180	17.7	1.6	38.3	<.05	.6	<.05	13.0
GW02-C	915	29.2	40.0	.82	<.2	6.9	.67	<.5	1.52	26.8
GW02-D	576	22.1	10.9	.28	<.2	1.1	.18	1.5	1.71	48.6
GW02-(I)	852	40.2	23.4	.42	.3	17.6	.57	<.5	<.05	31.9
GW02-(II)	986	44.1	26.4	.41	.3	14.2	.60	<.5	.10	34.1
GW02-(III)	639	39.9	20.5	.37	<.2	19.1	.45	<.5	.52	36.4
GW02-(IV)	576	46.4	28.1	.32	<.2	12.1	.35	<.5	.19	62.9
GW02-(V)-2	787	58.7	34.7	.31	<.2	6.6	.35	2.5	1.62	44.7
GW02-(V)-3	774	58.2	28.8	.30	<.2	6.5	.36	2.6	1.67	43.2
GW02-(VI)	1320	55.1	25.8	.27	<.2	2.4	.46	3.2	<.05	65.1
GW02-(VII)-2	1290	54.7	22.5	.24	<.2	1.9	.39	3.4	.52	67.3
GW02-(VII)-3	1280	55.5	22.9	.24	<.2	2.0	.40	3.6	.52	73.5
GW03-B	77.5	62.9	446	6.46	.2	97.1	<.05	.6	<.05	8.40
GW03-C-2	781	79.4	483	20.4	<.2	169	<.05	.6	<.05	8.41
GW03-E	278	61.9	294	14.4	<.2	108	<.05	.5	<.05	7.40
GW03-F	112	72.6	355	10.5	.2	104	<.05	.6	<.05	6.72
GW03-G	555	82.9	377	14.0	<.2	153	<.05	.6	<.05	8.85
GW04-A	1530	67.4	152	17.4	<.2	55.6	<.05	.8	<.05	11.9
GW04-B	1160	64.0	214	18.3	<.2	52.5	<.05	.6	<.05	8.62
GW04-C	75.6	61.2	271	10.1	<.2	61.8	.07	.6	<.05	6.65
GW04-D	152	65.1	244	6.78	.4	64.0	.07	.6	<.05	7.41
GW05-A	3880	80.4	215	12.7	<.2	36.5	<.05	.7	<.05	8.31
GW05-C-2	2280	66.5	215	17.4	<.2	47.0	<.05	.7	<.05	9.46
GW05-D	3190	21.6	98.3	4.12	<.2	8.8	<.05	.7	<.05	11.6
GW05-F	1220	43.6	77.6	2.50	<.2	18.3	<.05	.5	<.05	9.75
GW05-H	1010	42.3	290	6.82	<.2	17.5	<.05	.7	<.05	8.77
SW-1-2	784	18.8	100	7.04	<.2	18.9	.17	<.5	<.05	24.2
SW-1-3	770	18.7	100	7.37	<.2	18.2	.18	.5	<.05	23.1
SW-2-2	206	4.5	40.9	2.20	<.2	8.1	.18	<.5	<.05	15.6
SW-2-3	208	4.4	41.5	2.22	<.2	8.1	.17	<.5	<.05	15.5
CONTROL DATA	--	--	--	--	--	--	--	--	--	--
DET. LIMS.	.01	.5	.01	.01	.2	.5	.05	.5	.05	.05
BLANK	<.01	<.5	<.01	<.01	<.2	<.5	<.05	<.5	<.05	<.05
BLANK	<.01	<.5	<.01	<.01	<.2	<.5	<.05	<.5	<.05	<.05
GW02-C	915	29.2	40.0	.82	<.2	6.9	.67	<.5	1.52	26.8
GW02-C-R	912	29.3	40.2	.84	.3	6.8	.67	<.5	1.57	25.6
SW-2-2	206	4.5	40.9	2.20	<.2	8.1	.18	<.5	<.05	15.6

TABLE 3.2a: ANALYTICAL RESULTS FOR ANIONS AND CATIONS (measured by Barringer) (cont'd)

SAMPLE ID	FE MG/L	K MG/L	MG MG/L	MN MG/L	MO MG/L	NA MG/L	NI MG/L	P MG/L	PB MG/L	SI MG/L
SW-2-2-R	209	4.6	41.1	2.24	<.2	8.1	.18	<.5	<.05	16.5
GW04-C	--	--	--	--	--	--	--	--	<.05	--
GW04-C-R	--	--	--	--	--	--	--	--	--	--
CONTROL STD	.90	<.5	<.01	.21	<.2	<.5	.20	<.5	.24	<.05
CONTROL.EST.	1.00	--	--	.20	--	--	.20	--	.20	--
EPA STD	<.01	9.9	10.6	<.01	<.2	42.9	<.05	<.5	--	.38
EPA.STD(CRT)	--	10.0	10.0	--	--	40.0	--	--	--	--

TABLE 3.2a: ANALYTICAL RESULTS FOR ANIONS AND CATIONS (measured by Barringer) (cont'd)

SAMPLE ID	SR MG/L	TH MG/L	TI MG/L	V MG/L	ZN MG/L	ZR MG/L	PH	SP.COND. UMHOS/CM
GW01-A	.761	<.05	.194	<.005	.22	.48	3.41	7700
GW01-B-2	.971	<.05	.027	<.005	.34	.07	3.53	7490
GW01-B-3	.971	<.05	.029	<.005	.35	.07	3.60	7510
GW01-C	.800	<.05	.226	.021	.37	.65	3.69	6810
GW01-D	.687	1.80	.822	.124	.31	.05	2.47	6350
GW01-E	.407	.66	2.99	.091	.13	<.05	2.04	7730
GW02-A	.750	<.05	.046	.017	.14	.12	3.68	5070
GW02-B-2	1.00	.68	.329	.030	.74	.64	3.44	7960
GW02-B-3	.984	.66	.335	.030	.71	.68	3.51	7940
GW02-C	.607	.50	.209	.102	3.14	.43	3.66	4030
GW02-D	.334	.06	1.87	.051	.11	<.05	2.17	5740
GW02-(I)	.541	.15	.092	.113	.[illegible]	.18	3.40	4180
GW02-(II)	.575	.17	.093	.183	.[illegible]	.15	3.72	4570
GW02-(III)	.688	.05	.052	.272	.30	.10	3.87	3860
GW02-(IV)	.653	<.05	.040	.344	.56	.05	3.49	3870
GW02-(V)-2	.452	3.23	1.23	.109	.17	.05	2.41	4600
GW02-(V)-3	.451	3.21	1.21	.109	.17	.05	2.30	5770
GW02-(VI)	.336	3.29	3.18	.136	.18	.07	1.95	9690
GW02-(VII)-2	.304	2.79	4.36	.128	.21	.08	1.83	10900
GW02-(VII)-3	.308	2.82	4.43	.133	.22	.08	1.83	11100
GW03-B	1.14	<.05	.008	.025	.05	<.05	7.38	4670
GW03-C-2	1.06	<.05	<.005	.016	.09	<.05	4.07	6370
GW03-E	.973	<.05	<.005	.021	.07	<.05	3.52	4310
GW03-F	.801	<.05	.010	.027	.07	<.05	4.44	4290
GW03-G	.761	<.05	<.005	.021	.08	<.05	4.11	5010
GW04-A	.977	<.05	.019	.026	.16	.07	3.73	5370
GW04-B	1.27	<.05	.007	.016	.10	<.05	4.07	4910
GW04-C	.914	<.05	<.005	.027	.04	<.05	6.88	3700
GW04-D	.840	<.05	<.005	.014	.06	<.05	6.12	3600
GW05-A	1.10	<.05	.071	<.005	.24	.17	3.42	9080
GW05-C-2	1.42	<.05	.020	.007	.23	.07	3.58	6630
GW05-D	.994	<.05	.016	.008	.25	.05	3.38	6460
GW05-F	.919	<.05	.008	.013	.10	<.05	3.79	4440
GW05-H	.685	<.05	.010	.018	.12	<.05	3.84	4870
SW-1-2	.559	.06	.064	.019	.21	.15	2.81	3520
SW-1-3	.540	.07	.061	.020	.22	.15	2.83	3690
SW-2-2	.178	.37	.111	.017	.16	.06	2.73	2220
SW-2-3	.177	.36	.105	.017	.16	.06	2.74	2190
CONTROL DATA	--	--	--	--	--	--	--	--
DET. LIMS.	.001	.05	.005	.005	.01	.05	.01	1
BLANK	<.001	<.05	<.005	<.005	<.01	<.05	5.20	4
BLANK	.002	<.05	<.005	<.005	<.01	<.05	5.27	4
GW02-C	.607	.50	.209	.102	3.14	.43	3.66	4030
GW02-C-R	.587	.51	.198	.087	3.09	.40	3.67	4050
SW-2-2	.178	.37	.111	.017	.16	.06	2.73	2220

TABLE 3.2a: ANALYTICAL RESULTS FOR ANIONS AND CATIONS (measured by Barringer) (cont'd)

SAMPLE ID	SR MG/L	TH MG/L	TI MG/L	V MG/L	ZN MG/L	ZR MG/L	PH	SP.COND. UMHOS/Cm
SW-2-2-R	.181	.36	.117	.014	.17	.06	--	--
GW04-C	--	--	--	--	--	--	6.88	3700
GW04-C-R	--	--	--	--	--	--	6.91	3680
CONTROL STD	.199	<.05	.204	.185	.20	.19	4.48	12600
CONTROL.EST.	.200	--	.200	.200	.20	.20	4.45	12900
EPA STD	.031	<.05	<.005	.010	.07	<.05	--	--
EPA.STD(CRT)	--	--	--	--	--	--	--	--

TABLE 3.2a: ANALYTICAL RESULTS FOR ANIONS AND CATIONS (measured by Barringer) (cont'd)

SAMPLE ID	F- MG/L	CL- MG/L	NO2-N MG/L	BR- MG/L	NO3-N MG/L	PO4-3 MG/L	SO4= MG/L
GW01-A	<1	<1	<1	<5	<1	<10	8480
GW01-B-2	<1	32	<1	<5	<1	<10	8350
GW01-B-3	<1	<1	<1	<5	<1	<10	8020
GW01-C	2	28	<1	<5	<1	<10	7400
GW01-D	<1	<1	<1	<5	<1	<10	5080
GW01-E	<1	<1	<1	<5	<1	<10	4300
GW02-A	<1	<1	<1	<5	<1	<10	4480
GW02-B-2	<1	47	<1	<5	<1	<10	9040
GW02-B-3	<1	42	<1	<5	<1	<10	9080
GW02-C	<1	<1	<1	<5	<1	<10	3620
GW02-D	<1	<1	<1	<5	<1	<10	3640
GW02-(I)	<1	<1	<1	<5	<1	<10	3790
GW02-(II)	<1	32	<1	<5	<1	<10	4510
GW02-(III)	<1	42	<1	<5	<1	<10	3520
GW02-(IV)	<1	<1	<1	<5	<1	<10	3590
GW02-(V)-2	3	<1	<1	<5	<1	<10	4370
GW02-(V)-3	3	<1	<1	<5	<1	<10	4310
GW02-(VI)	<1	<1	<1	<5	<1	<10	5640
GW02-(VII)-2	2	<1	<1	<5	<1	<10	6040
GW02-(VII)-3	<1	<1	<1	<5	<1	<10	6040
GW03-B	2	99	<1	<5	<1	<10	3060
GW03-C-2	<1	234	<1	<5	<1	<10	5170
GW03-E	1	148	<1	<5	<1	<10	3140
GW03-F	1	159	<1	<5	<1	<10	3140
GW03-G	<1	115	<1	<5	<1	<10	3250
GW04-A	<1	46	<1	<5	<1	<10	4610
GW04-B	1	48	<1	<5	<1	<10	3960
GW04-C	3	45	<1	<5	<1	<10	2440
GW04-D	2	58	<1	<5	<1	<10	2490
GW05-A	<1	40	<1	<5	<1	<10	10500
GW05-C-2	<1	58	<1	<5	<1	<10	6270
GW05-D	<1	<1	<1	<5	<1	<10	6290
GW05-F	<1	36	<1	<5	<1	<10	3730
GW05-H	1	24	<1	<5	<1	<10	4180
SW-1-2	<1	<1	<1	<5	<1	<10	2870
SW-1-3	<1	<1	<1	<5	<1	<10	2930
SW-2-2	<1	<1	<1	<5	<1	<10	1420
SW-2-3	<1	<1	<1	<5	<1	<10	1320
CONTROL DATA	--	--	--	--	--	--	--
DET. LIMS.	1	1	1	5	1	10	5
BLANK	<1	<1	<1	<5	<1	<10	<5
BLANK	<1	<1	<1	<5	<1	<10	<5
GW02-C	<1	<1	<1	<5	<1	<10	3620
GW02-C-R	<1	<1	<1	<5	<1	<10	3560
SW-2-2	<1	<1	<1	<5	<1	<10	1420

TABLE 3.2a: ANALYTICAL RESULTS FOR ANIONS AND CATIONS (measured by Barringer) (cont'd)

SAMPLE ID	F- MG/L	CL- MG/L	NO2-N MG/L	BR- MG/L	NO3-N MG/L	PO4-3 MG/L	SO4= MG/L
SW-2-2-R	--	--	--	--	--	--	--
GW04-C	3	45	<1	<5	<1	<10	2440
GW04-C-R	3	46	<1	<5	<1	<10	2400
CONTROL STD	--	50	--	--	--	--	50
CONTROL.EST.	--	50	--	--	--	--	50
EPA STD	--	--	--	--	--	--	--
EPA.STD(CRT)	--	--	--	--	--	--	--

TABLE 3.2a: ANALYTICAL RESULTS FOR ANIONS AND CATIONS (measured by Barringer) (cont'd)

SAMPLE ID	AG MG/L	AL MG/L	B MG/L	BA MG/L	BE MG/L	CA MG/L	CD MG/L	CO MG/L	CR MG/L
GW-LAB-1	<.005	.02	<.004	<.005	<.0005	.04	<.01	<.05	<.01
GW-LAB-2	<.005	.05	<.004	<.005	<.0005	.08	<.01	.06	<.01
GW-FIELD-1	<.005	<.01	<.004	<.005	<.0005	.33	<.01	<.05	<.01
GW-FIELD-2	<.005	<.01	<.004	<.005	<.0005	.04	<.01	<.05	<.01
GW-FIELD-3	<.005	<.01	<.004	<.005	<.0005	.16	<.01	<.05	<.01
GW-FIELD-4	<.005	<.01	<.004	<.005	<.0005	.12	<.01	<.05	<.01
CONTROL DATA	--	--	--	--	--	--	--	--	--
DET. LIMS.	.005	.01	.004	.005	.0005	.01	.01	.05	.01
BLANK	<.005	.02	<.004	<.005	<.0005	.08	<.01	<.05	<.01
GW-LAB-1	<.005	.02	<.004	<.005	<.0005	.04	<.01	<.05	<.01
GW-LAB-1-R	<.005	.01	<.004	<.005	<.0005	.04	<.01	<.05	<.01
GW-LAB-2	<.005	.05	<.004	<.005	<.0005	.08	<.01	.06	<.01
GW-LAB-2-R	<.005	.05	<.004	<.005	<.0005	.12	<.01	.08	<.01
CONTROL STD	.007	1.00	.199	.957	.0189	<.01	.20	.23	.19
CONTROL.EST.	--	1.00	.200	--	.0200	--	.20	.20	.20

SAMPLE ID	CU MG/L	FE MG/L	K MG/L	MG MG/L	MN MG/L	MO MG/L	NA MG/L	NI MG/L	P MG/L
GW-LAB-1	<.008	40.2	<.5	<.01	.04	<.2	<.5	<.05	<.5
GW-LAB-2	.010	403	<.5	.04	.45	<.2	<.5	<.05	<.5
GW-FIELD-1	<.008	.61	<.5	.06	<.01	<.2	<.5	<.05	<.5
GW-FIELD-2	<.008	.03	<.5	<.01	<.01	<.2	<.5	<.05	<.5
GW-FIELD-3	<.008	<.01	<.5	<.01	<.01	<.2	<.5	<.05	<.5
GW-FIELD-4	<.008	.03	<.5	<.01	<.01	<.2	<.5	<.05	<.5
CONTROL DATA	--	--	--	--	--	--	--	--	--
DET. LIMS.	.008	.01	.5	.01	.01	.2	.5	.05	.5
BLANK	<.008	<.01	<.5	<.01	<.01	<.2	<.5	<.05	<.5
GW-LAB-1	<.008	40.2	<.5	<.01	.04	<.2	<.5	<.05	<.5
GW-LAB-1-R	<.008	40.0	<.5	<.01	.04	<.2	<.5	<.05	<.5
GW-LAB-2	.010	403	<.5	.04	.45	<.2	<.5	<.05	<.5
GW-LAB-2-R	.010	400	<.5	.05	.46	<.2	<.5	<.05	<.5
CONTROL STD	.194	1.01	<.5	<.01	.20	<.2	<.5	.21	<.5
CONTROL.EST.	.200	1.00	--	--	.20	--	--	.20	--

TABLE 3.2a: ANALYTICAL RESULTS FOR ANIONS AND CATIONS (measured by Barringer) (cont'd)

SAMPLE ID	PB MG/L	SI MG/L	SR MG/L	TH MG/L	TI MG/L	V MG/L	ZN MG/L	ZR MG/L
GW-LAB-1	<.05	<.05	<.001	<.05	<.005	<.005	<.01	<.05
GW-LAB-2	<.05	<.05	<.001	<.05	<.005	<.005	.03	<.05
GW-FIELD-1	<.05	<.05	.002	<.05	<.005	<.005	<.01	<.05
GW-FIELD-2	<.05	<.05	.002	<.05	<.005	<.005	<.01	<.05
GW-FIELD-3	<.05	<.05	.002	<.05	<.005	<.005	<.01	<.05
GW-FIELD-4	<.05	<.05	.002	<.05	<.005	<.005	<.01	<.05
CONTROL DATA	--	--	--	--	--	--	--	--
DET. LIMS.	.05	.05	.001	.05	.005	.005	.01	.05
BLANK	<.05	<.05	.002	<.05	<.005	.008	<.01	<.05
GW-LAB-1	<.05	<.05	<.001	<.05	<.005	<.005	<.01	<.05
GW-LAB-1-R	<.05	<.05	<.001	<.05	<.005	<.005	<.01	<.05
GW-LAB-2	<.05	<.05	<.001	<.05	<.005	<.005	.04	<.05
GW-LAB-2-R	<.05	<.05	<.001	<.05	<.005	.006	.03	<.05
CONTROL STD	.99	<.05	.195	<.05	.194	.187	.21	.18
CONTROL.EST.	1.00	--	.200	--	.200	.200	.20	.20

SAMPLE ID	F- MG/L	CL- MG/L	NO2-N MG/L	BR- MG/L	NO3-N MG/L	PO4-3 MG/L	SO4= MG/L
GW-LAB-1	<1	<1	<1	<5	1910	<10	<5
GW-LAB-2	<1	<1	<1	<5	1950	<10	404
GW-FIELD-1	--	--	--	--	--	--	--
GW-FIELD-2	--	--	--	--	--	--	--
GW-FIELD-3	--	--	--	--	--	--	--
GW-FIELD-4	--	--	--	--	--	--	--
CONTROL DATA	--	--	--	--	--	--	--
DET. LIMS.	1	1	1	5	1	10	5
BLANK	<1	<1	<1	<5	<1	<10	<5
GW-LAB-1	<1	<1	<1	<5	1910	<10	<5
GW-LAB-1-R	<1	<1	<1	<5	1880	<10	<5
GW-LAB-2	<1	<1	<1	<5	1950	<10	404
GW-LAB-2-R	--	--	--	--	--	--	--
CONTROL STD	--	50	--	--	5	--	50
CONTROL.EST.	--	50	--	--	5	--	50

APPENDIX C.2

GRAPHS SHOWING ANALYTICAL PRECISION FROM SPLIT DUPLICATES AND ANALYTICAL BIAS

Figures 3.1 to 3.5: Duplicate-Duplicate Plots Describing Analytical Precision From First Submission (Figure 3.1 is Given in Main Body)

Plotting Symbol:	BAR = 1
Plotting Symbol:	ERI = 2
Plotting Symbol:	SRC = 3
Plotting Symbol:	BEQ = 4
Plotting Symbol:	MON = 5

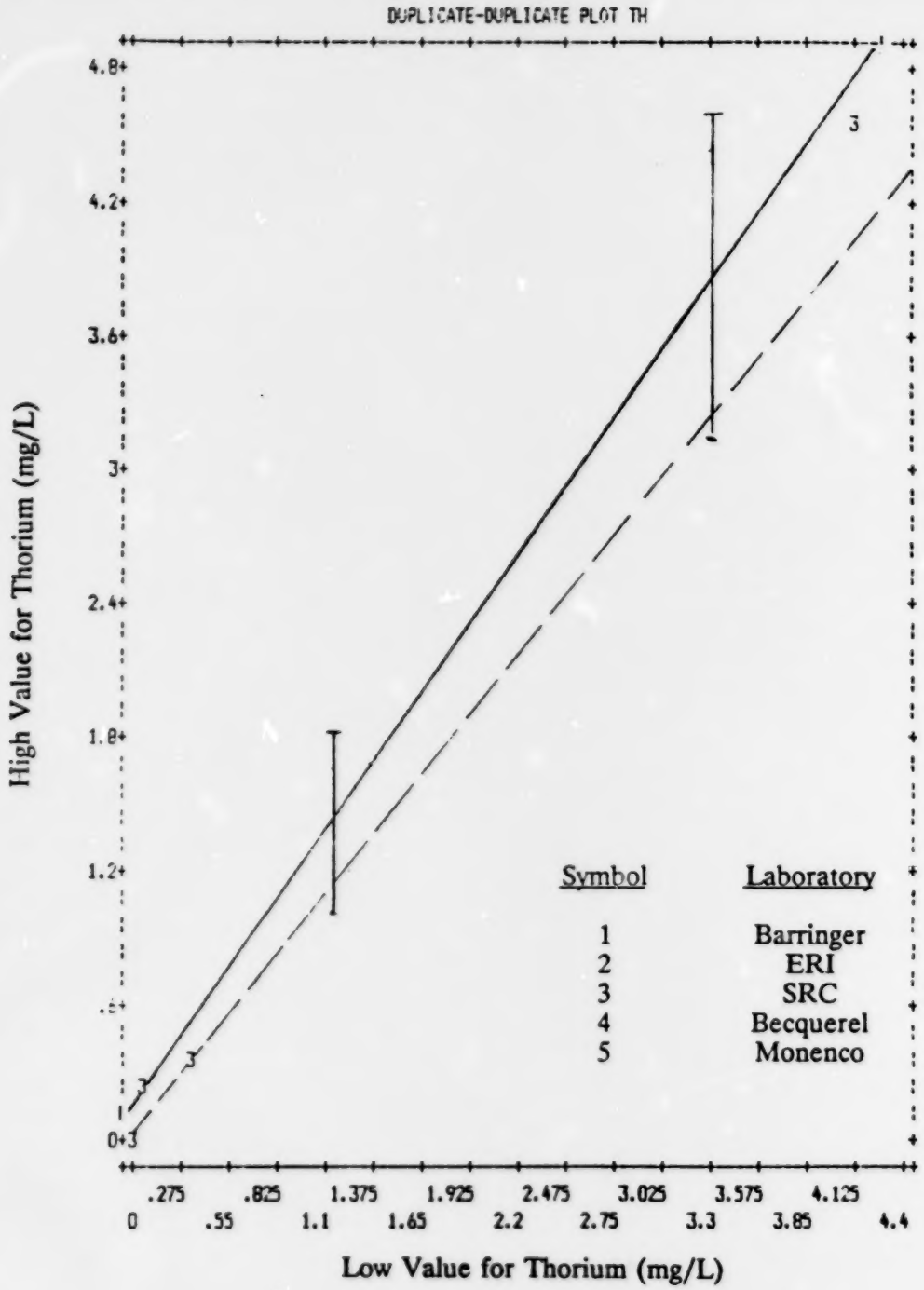
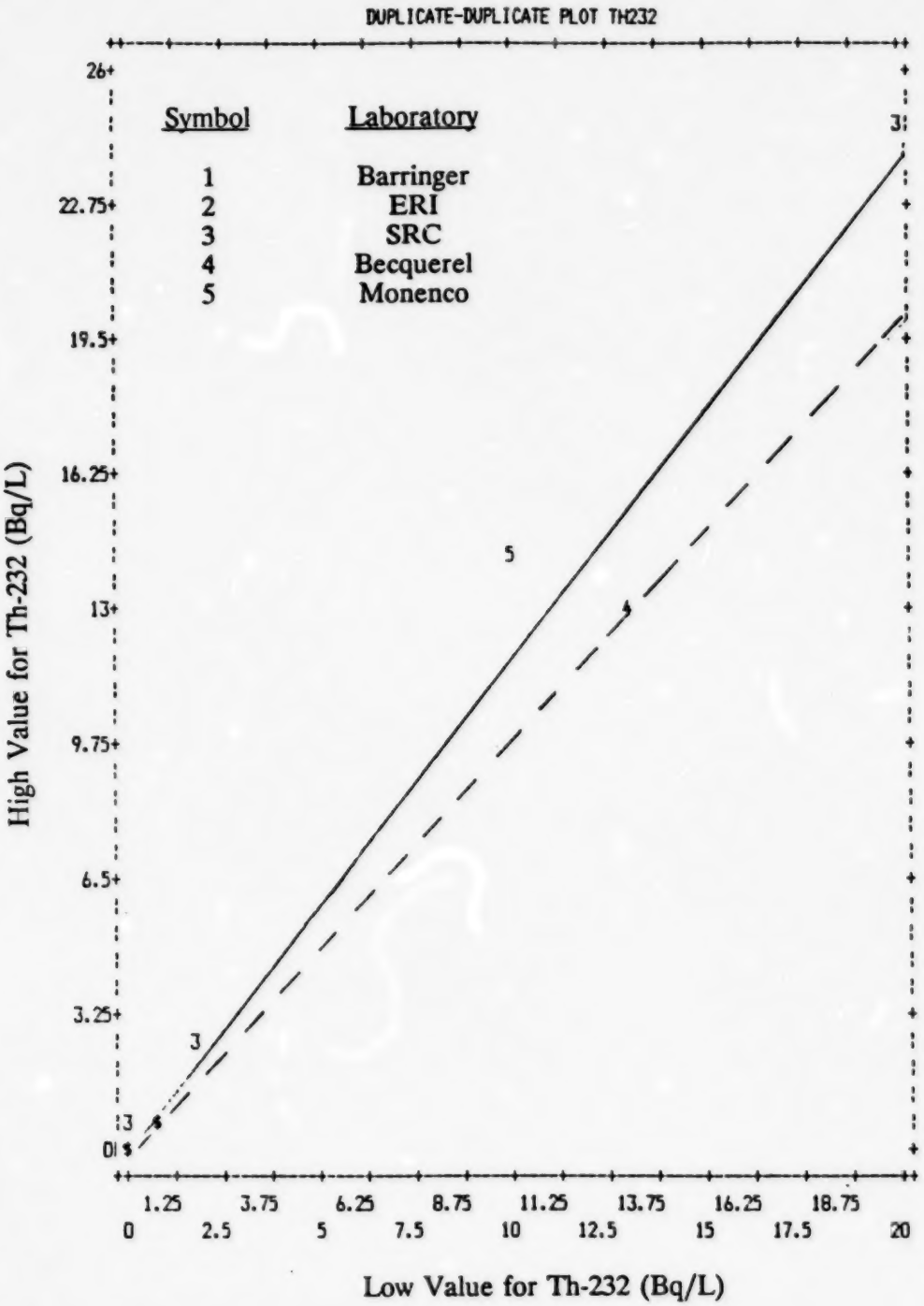
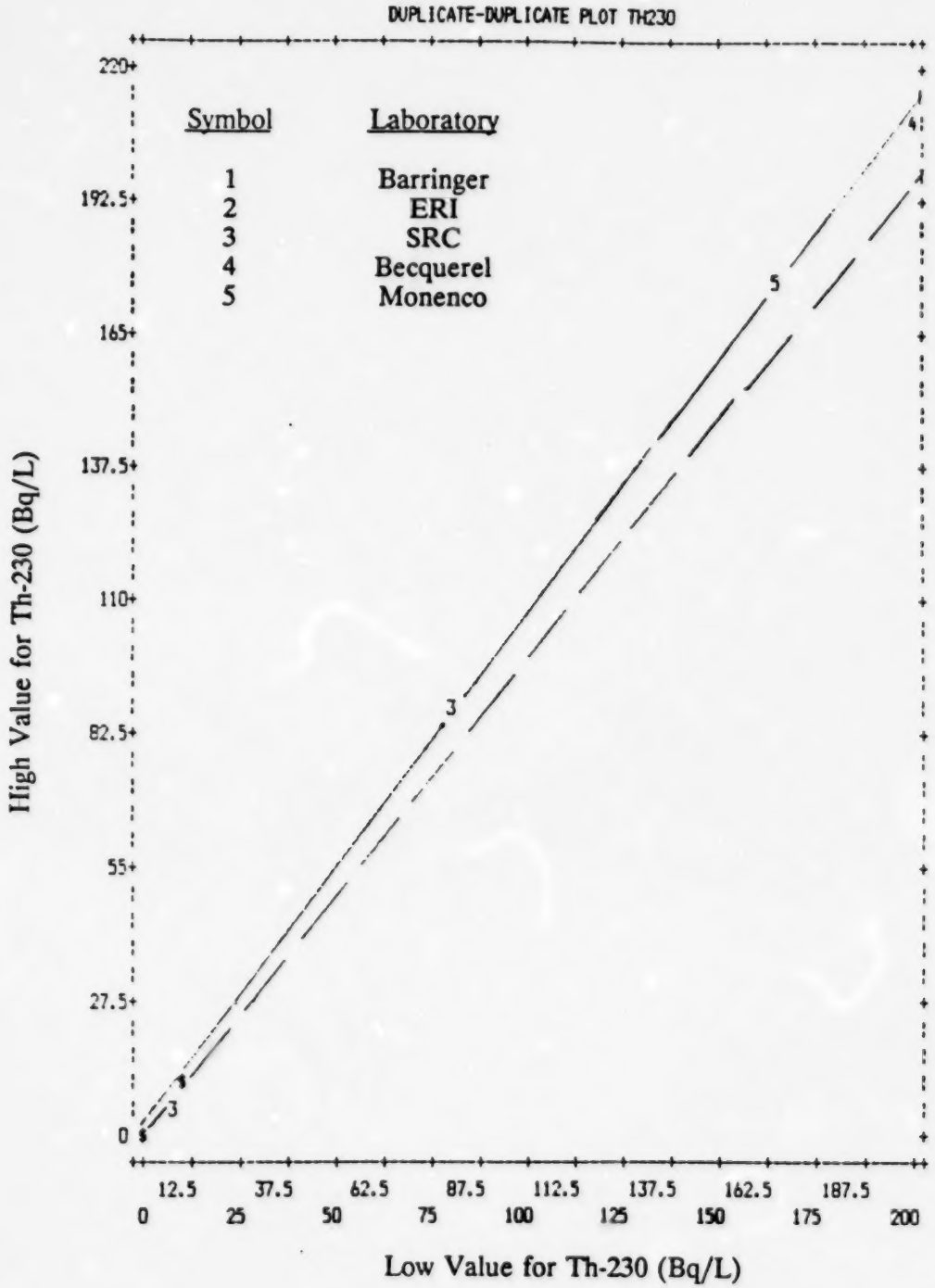


FIGURE 3.1: DUPLICATE-DUPLICATE PLOT FOR THORIUM
(dashed line represents perfect precision, solid line SRC)



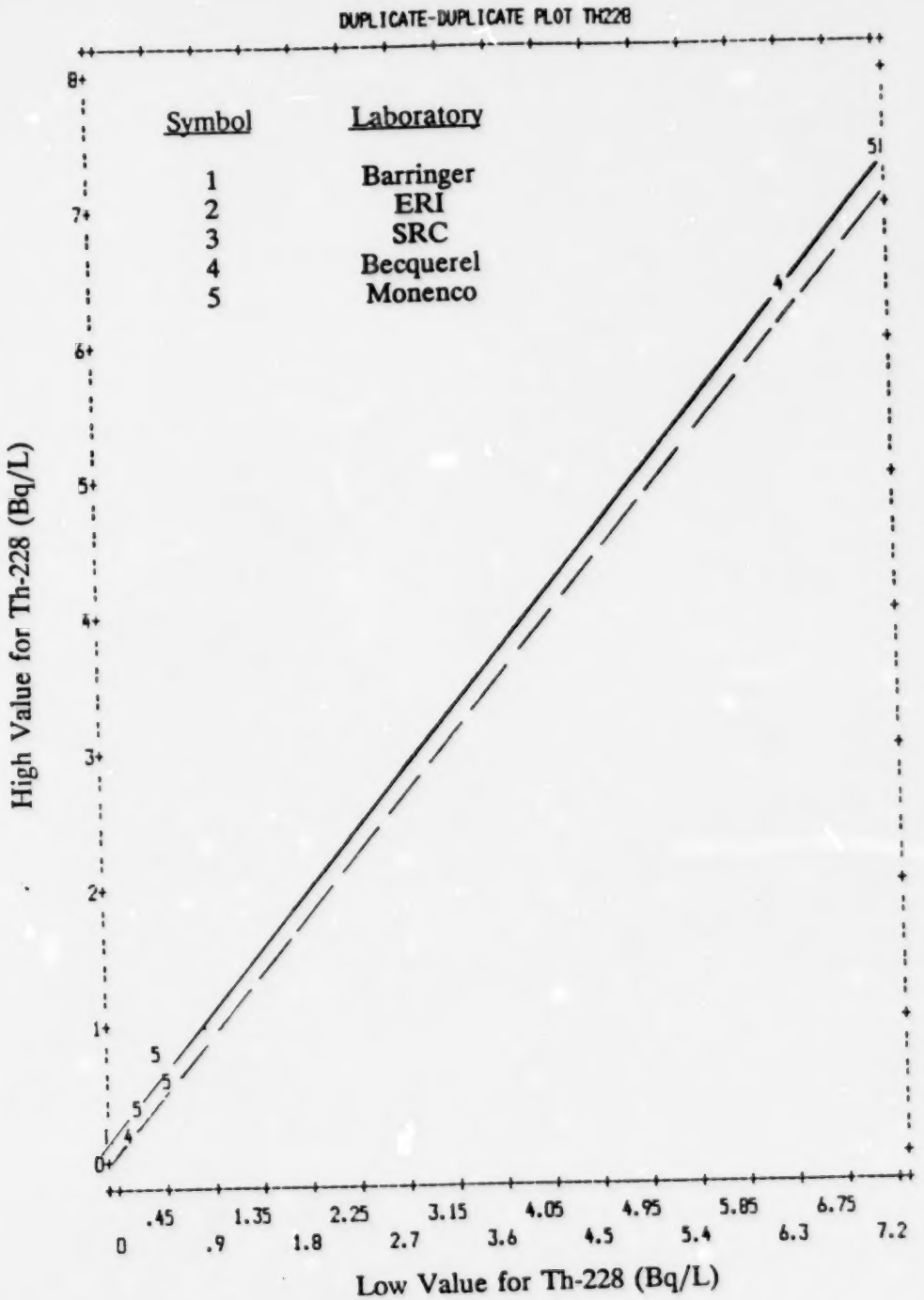
12 cases plotted. Regression statistics of HIGH on LOW:
Correlation .99158 R Squared .98324 S.E. of Est 1.10462 2-tailed Sig. .0000
Intercept(S.E.) .10936(.37188) Slope(S.E.) 1.20284(.04967)
Use first digit of LABNO as plotting symbol and $ for multiple occurrence.

FIGURE 3.2: DUPLICATE-DUPLICATE PLOT FOR TH-232
(solid line represents the group of three main laboratories, dashed line perfect precision)



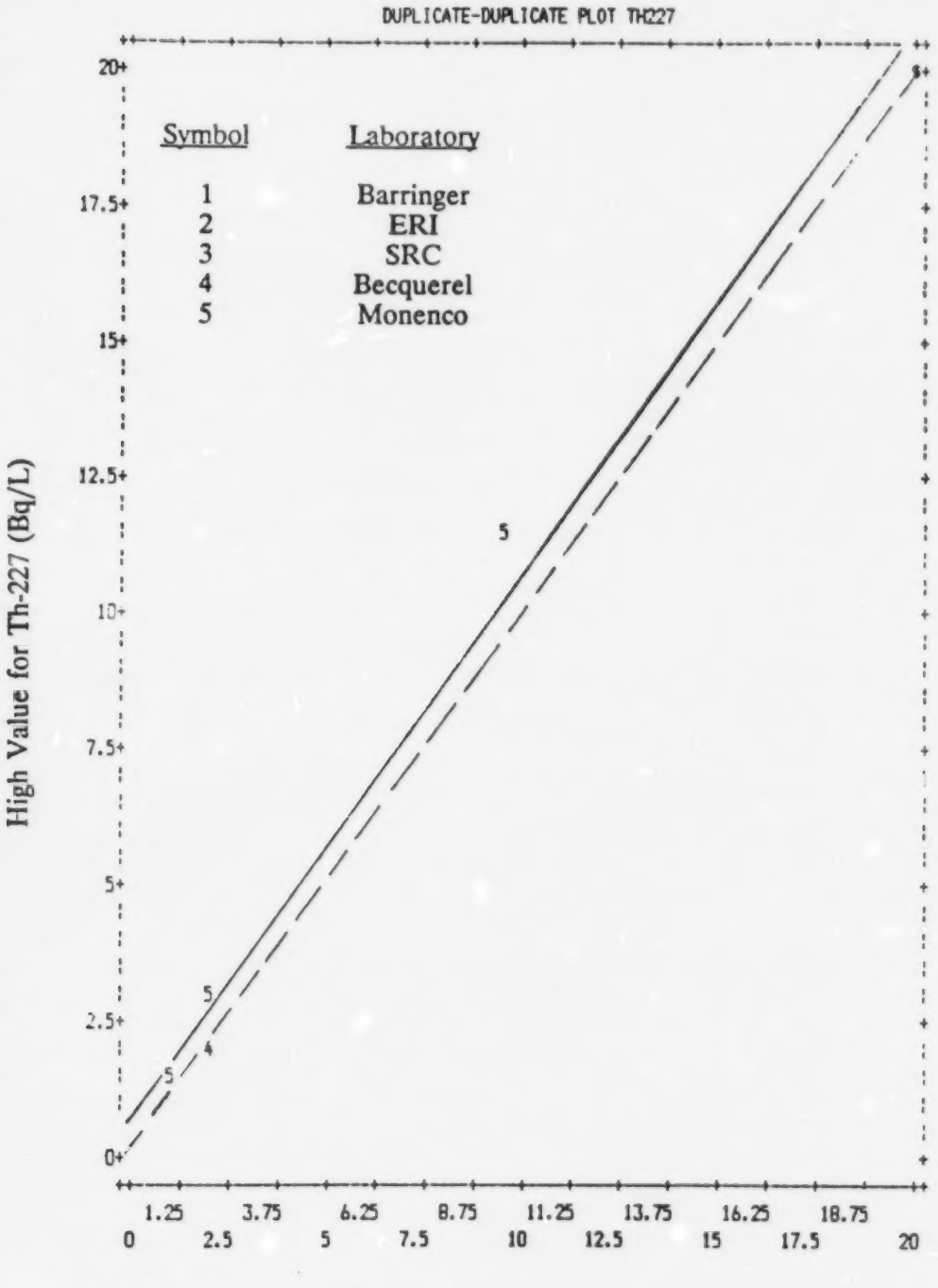
10 cases plotted. Regression statistics of HIGH on LOW:
Correlation .99974 R Squared .99947 S.E. of Est 1.95746 2-tailed Sig. .0000
Intercept(S.E.) .42439(.74128) Slope(S.E.) 1.05979(.00861)
Use first digit of LABNO as plotting symbol and $ for multiple occurrence.

FIGURE 3.3: DUPLICATE-DUPLICATE PLOT FOR TH-230
(soild line represents the group of three main laboratories, dashed line perfect precision)



8 cases plotted. Regression statistics of HIGH on LOW:
Correlation .99900 R Squared .99801 S.E. of Est .14676 2-tailed Sig. .0000
Intercept(S.E.) .12045(.06179) Slope(S.E.) .99907(.01823)
Use first digit of LABNO as plotting symbol and * for multiple occurrence.

FIGURE 3.4: DUPLICATE-DUPLICATE PLOT FOR TH-228
(solid line represents the two participating laboratories, dashed line perfect precision)



8 cases plotted. Regression statistics of HIGH on LOW:
Correlation .99675 R Squared .99351 S.E. of Est .77016 2-tailed Sig. .0000
Intercept(S.E.) .66259(.41172) Slope(S.E.) .97780(.03225)
Use first digit of LABNO as plotting symbol and $ for multiple occurrence.

FIGURE 3.5: DUPLICATE-DUPLICATE PLOT FOR TH-227
(solid line represents the two participating laboratories, dashed line perfect precision)

Figures 3.6 to 3.8: Duplicate-Duplicate Plots Describing Analytical Precision for the Second Sample Submission (Figure 3.6 is Given in Main Body)

Plotting Symbol:	BAR = 1
Plotting Symbol:	ERI = 2
Plotting Symbol:	SRC = 3
Plotting Symbol:	BEQ = 4
Plotting Symbol:	MON = 5

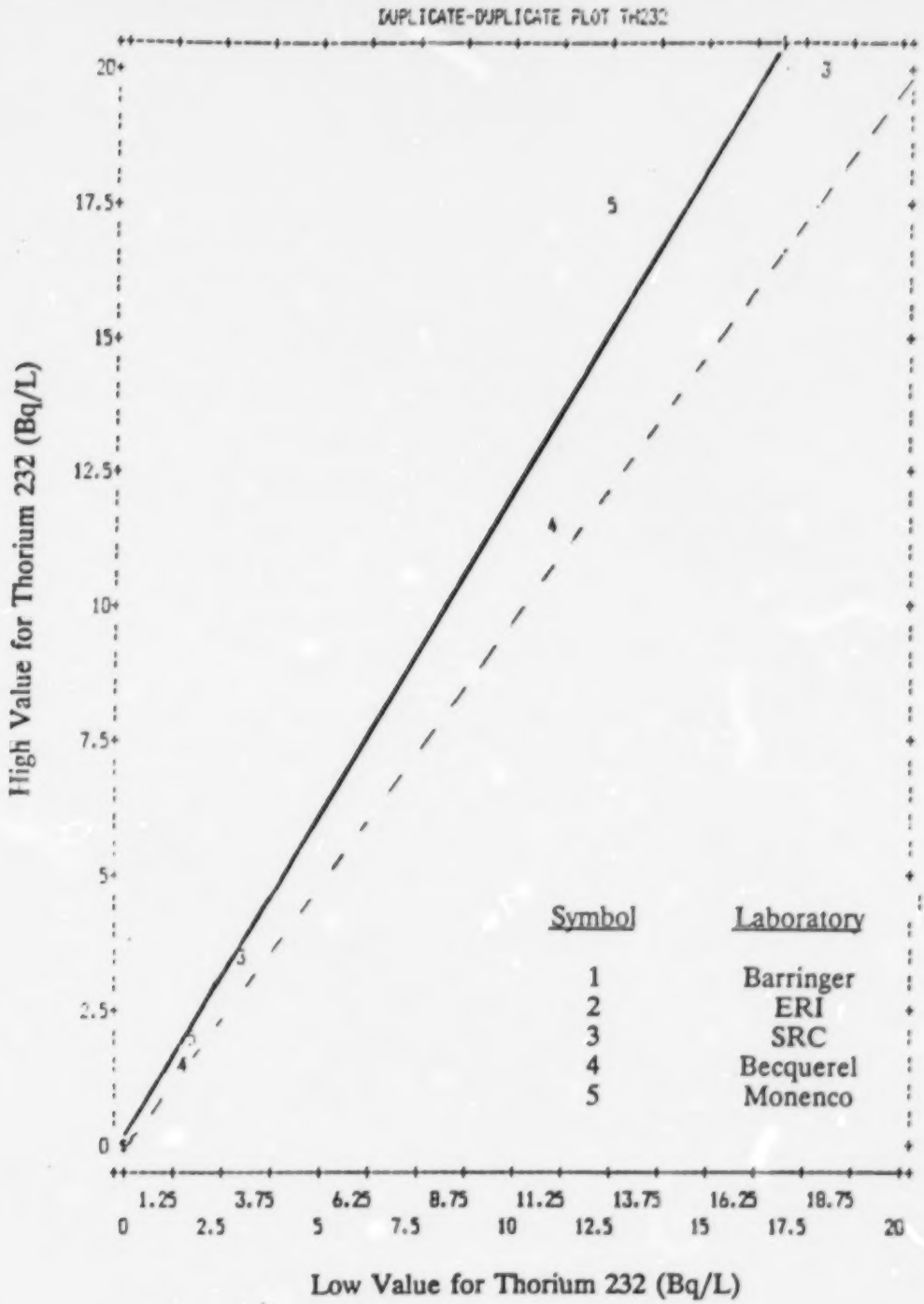


FIGURE 3.6: DUPLICATE-DUPLICATE PLOT FOR TH-232
(solid line represents the group of three main laboratories, dashed line perfect precision)

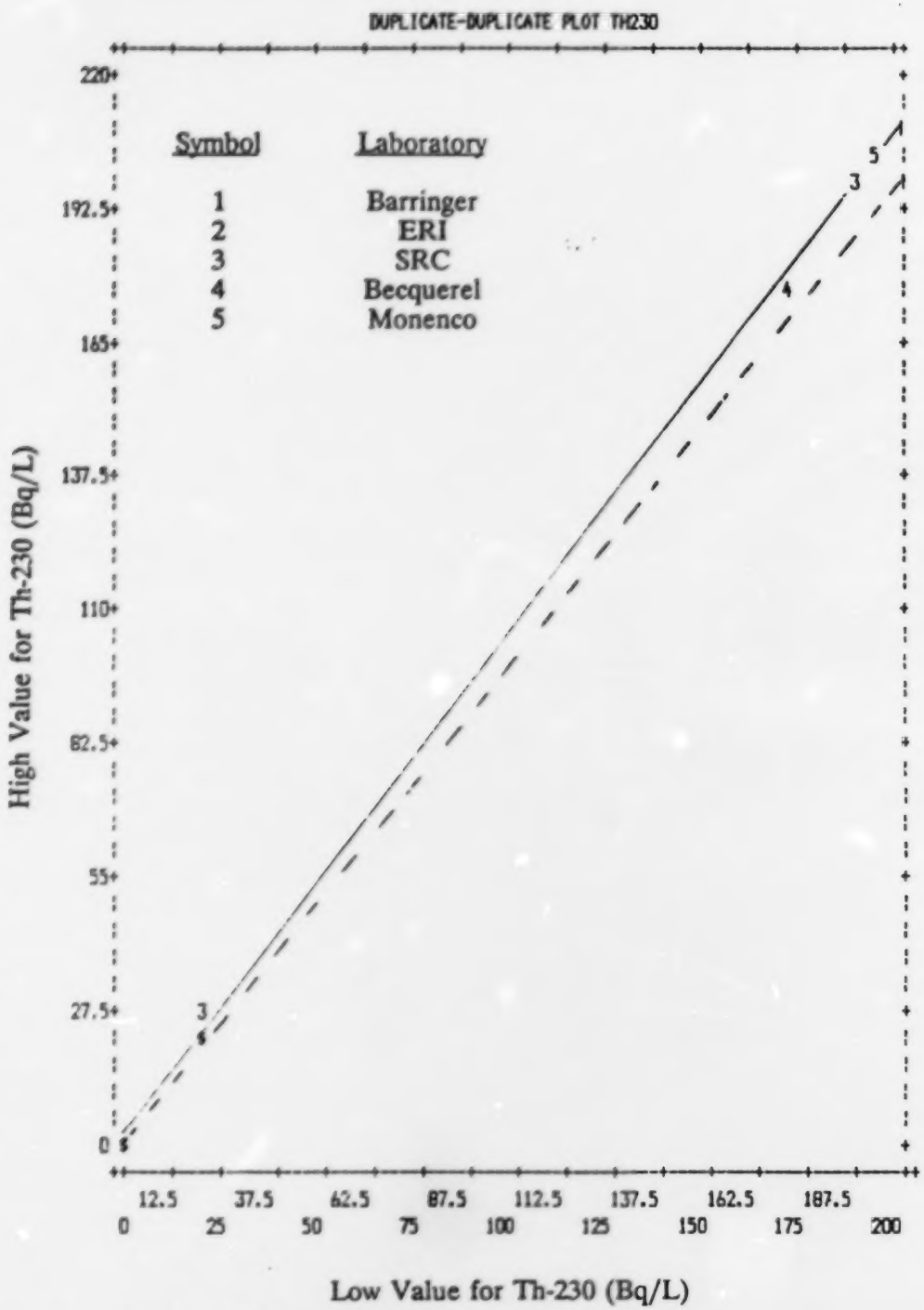
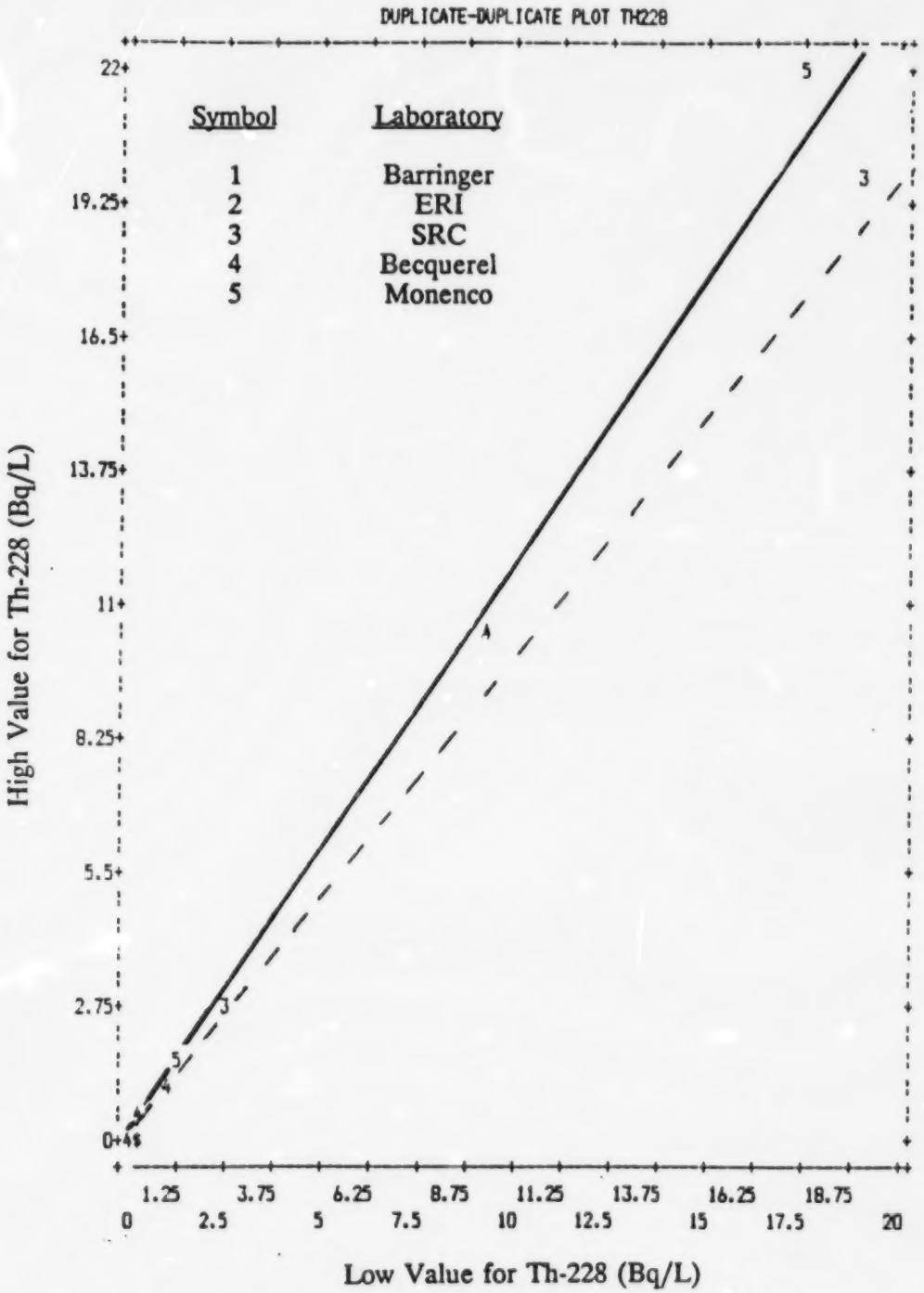


FIGURE 3.7: DUPLICATE-DUPLICATE PLOT FOR TH-230
(solid line represents the group of three main laboratories, dashed line perfect precision)



12 cases plotted. Regression statistics of HIGH on LOW:
Correlation .99546 R Squared .99094 S.E. of Est .80015 2-tailed Sig. .0000
Intercept(S.E.) -.01659(.27387) Slope(S.E.) 1.13772(.03440)
Use first digit of LABNO as plotting symbol and $ for multiple occurrence.

FIGURE 3.8: DUPLICATE-DUPLICATE PLOT FOR TH-228
(solid line represents the group of three main laboratories, dashed line perfect precision)

Figures 3.13 to 3.19: Figures Showing Youden-Paired Sample Plots for Examining Analytical Bias From First Sample Submission (Figure 3.12 is Given in Main Body)

Plotting Symbol:	BAR = 1
Plotting Symbol:	ERI = 2
Plotting Symbol:	SRC = 3
Plotting Symbol:	BEQ = 4
Plotting Symbol:	MON = 5

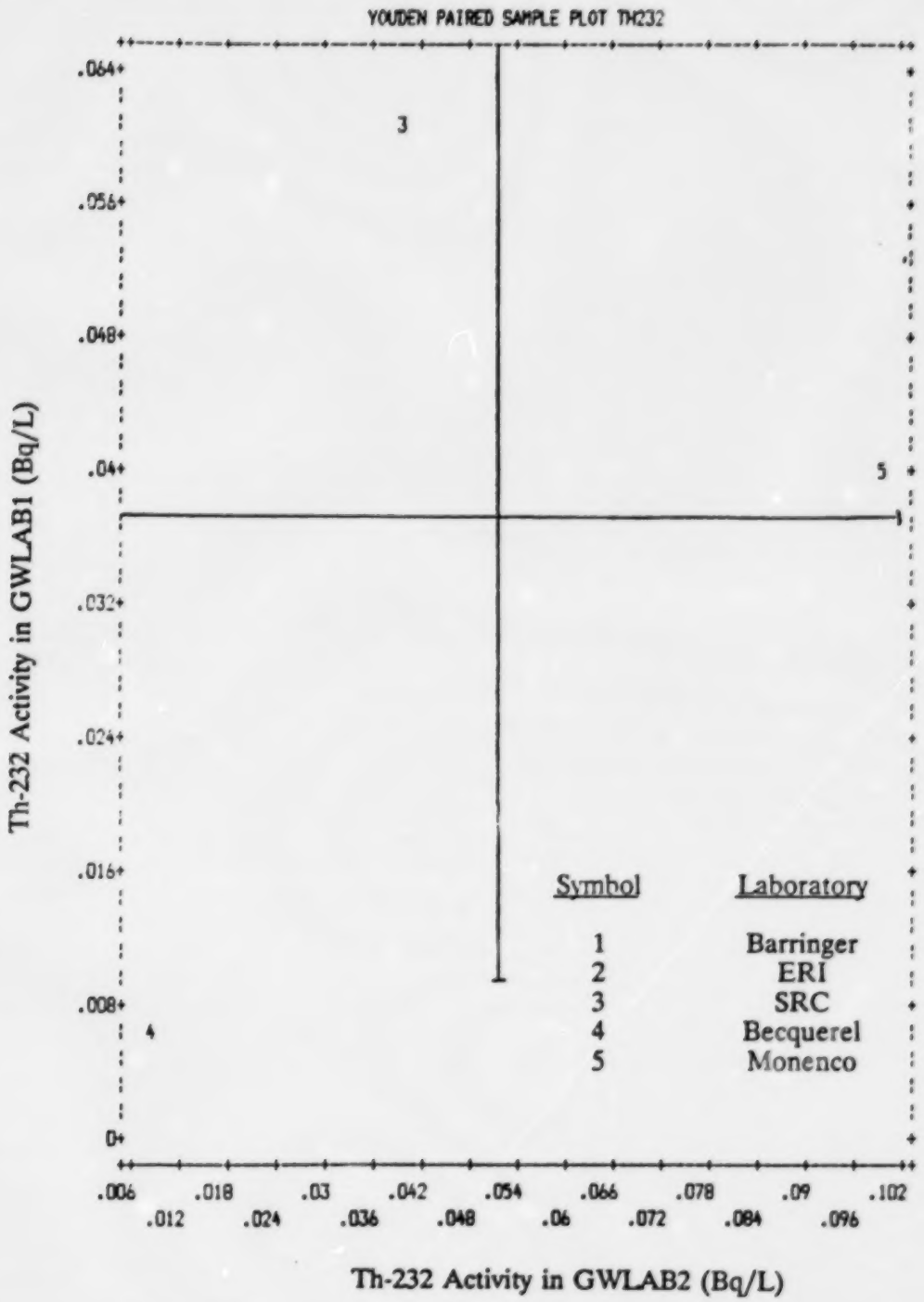


FIGURE 3.12: PAIRED SAMPLE PLOT OF TH-232 IN SYNTHETIC SAMPLES GWLAB1 AND GWLAB2 (crossbars show interlaboratory SD)

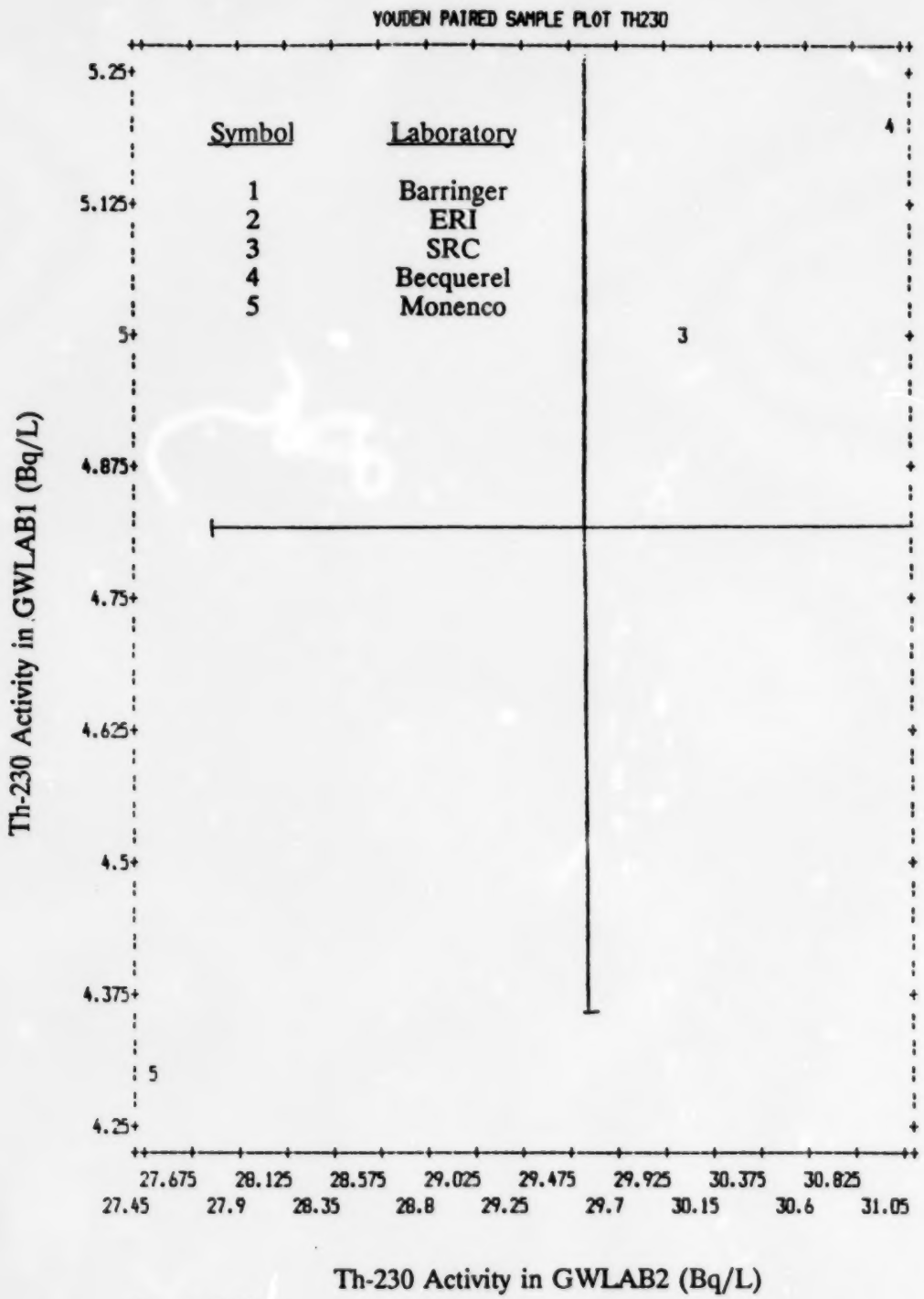


FIGURE 3.13: PAIRED SAMPLE PLOT OF TH-230 IN SYNTHETIC SAMPLES GWLAB1 AND GWLAB2 (crossbars show interlaboratory SD)

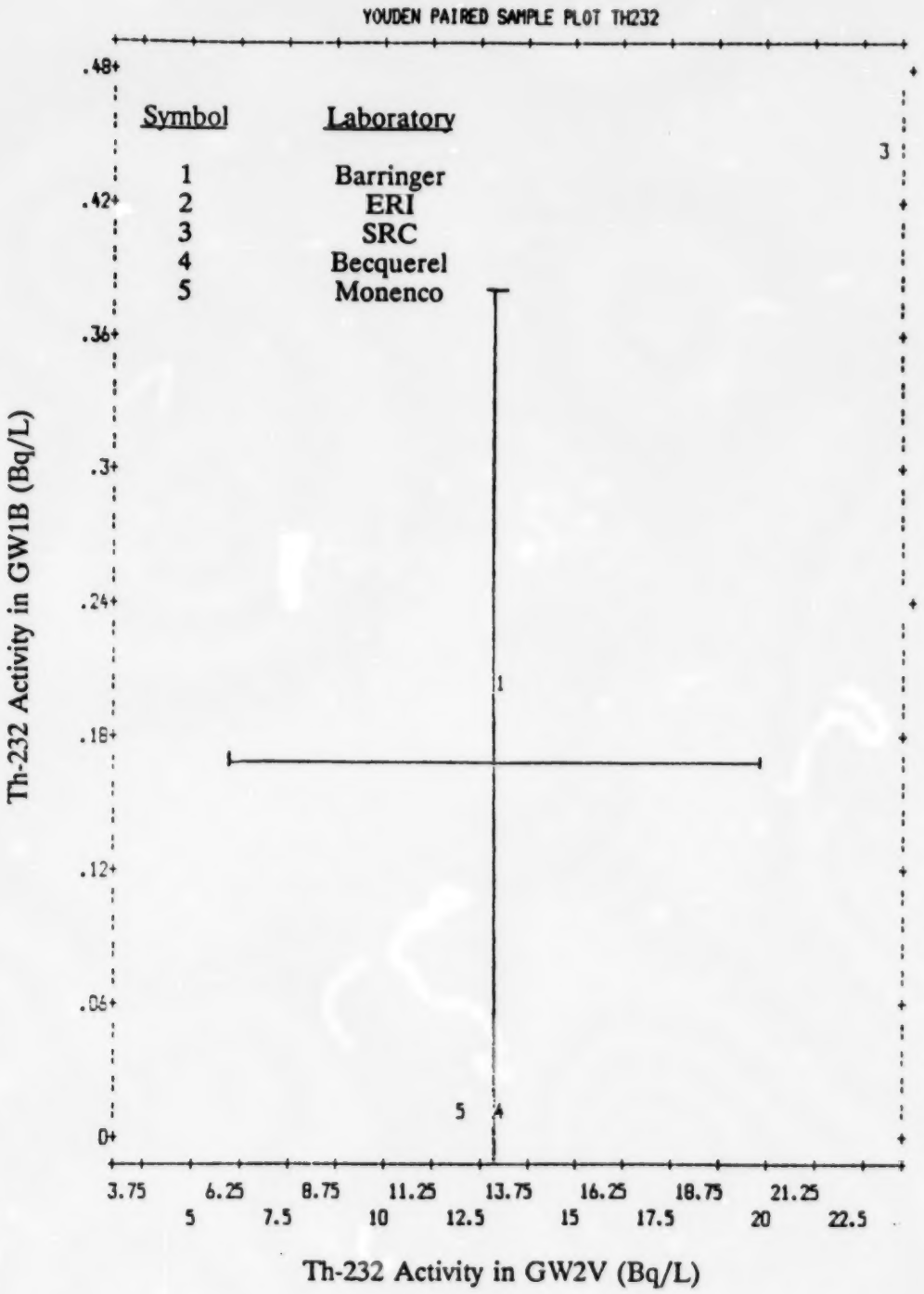
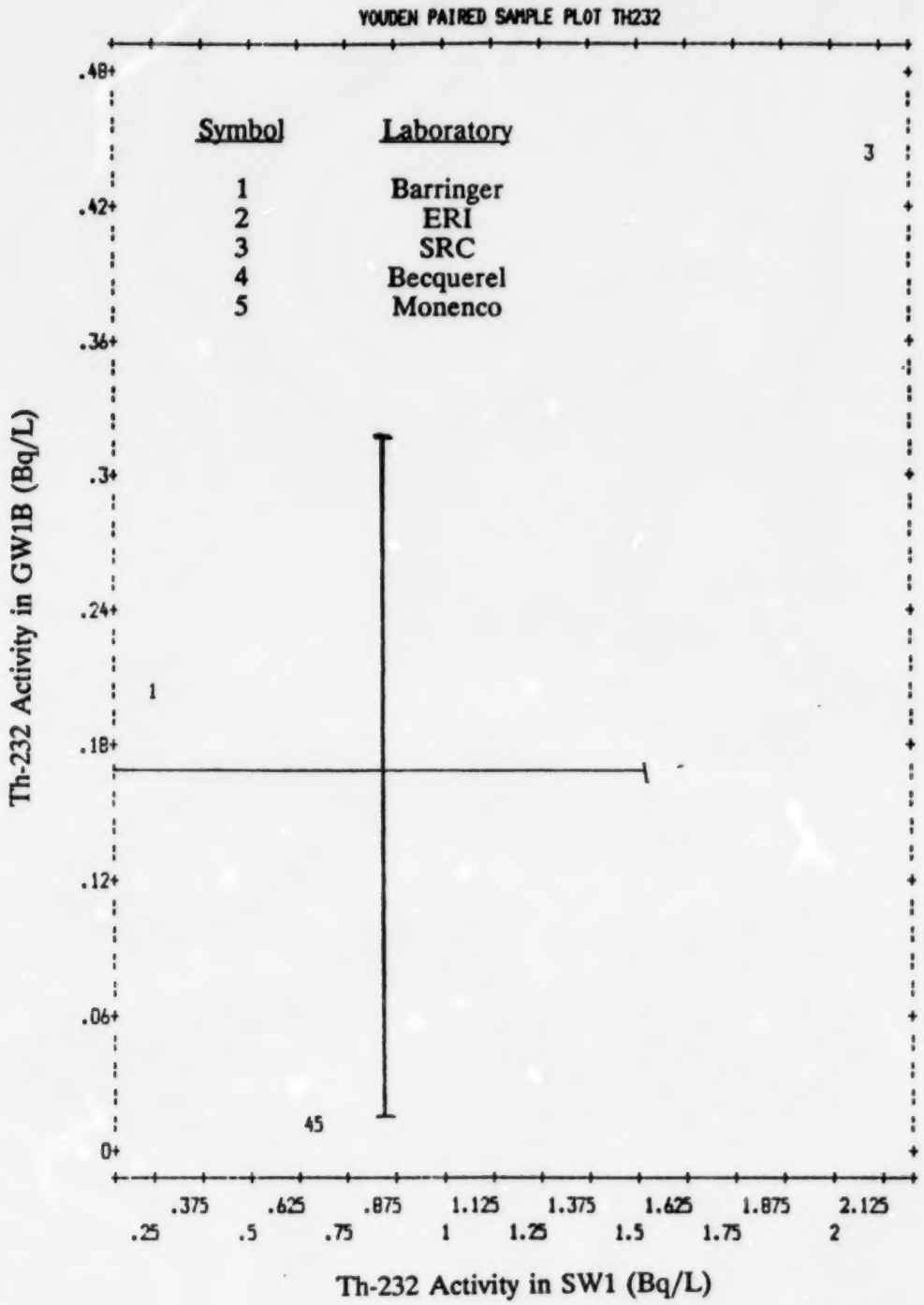


FIGURE 3.14: PAIRED SAMPLE PLOT OF TH-232 IN NATURAL SAMPLES GW1B AND SW1 (crossbars show interlaboratory SD)



4 cases plotted.
Use first digit of LABNO as plotting symbol and * for multiple occurrence.

FIGURE 3.15: PAIRED SAMPLE PLOT OF TH-232 IN NATURAL SAMPLES GW1B AND SW1 (crossbars show interlaboratory SD)

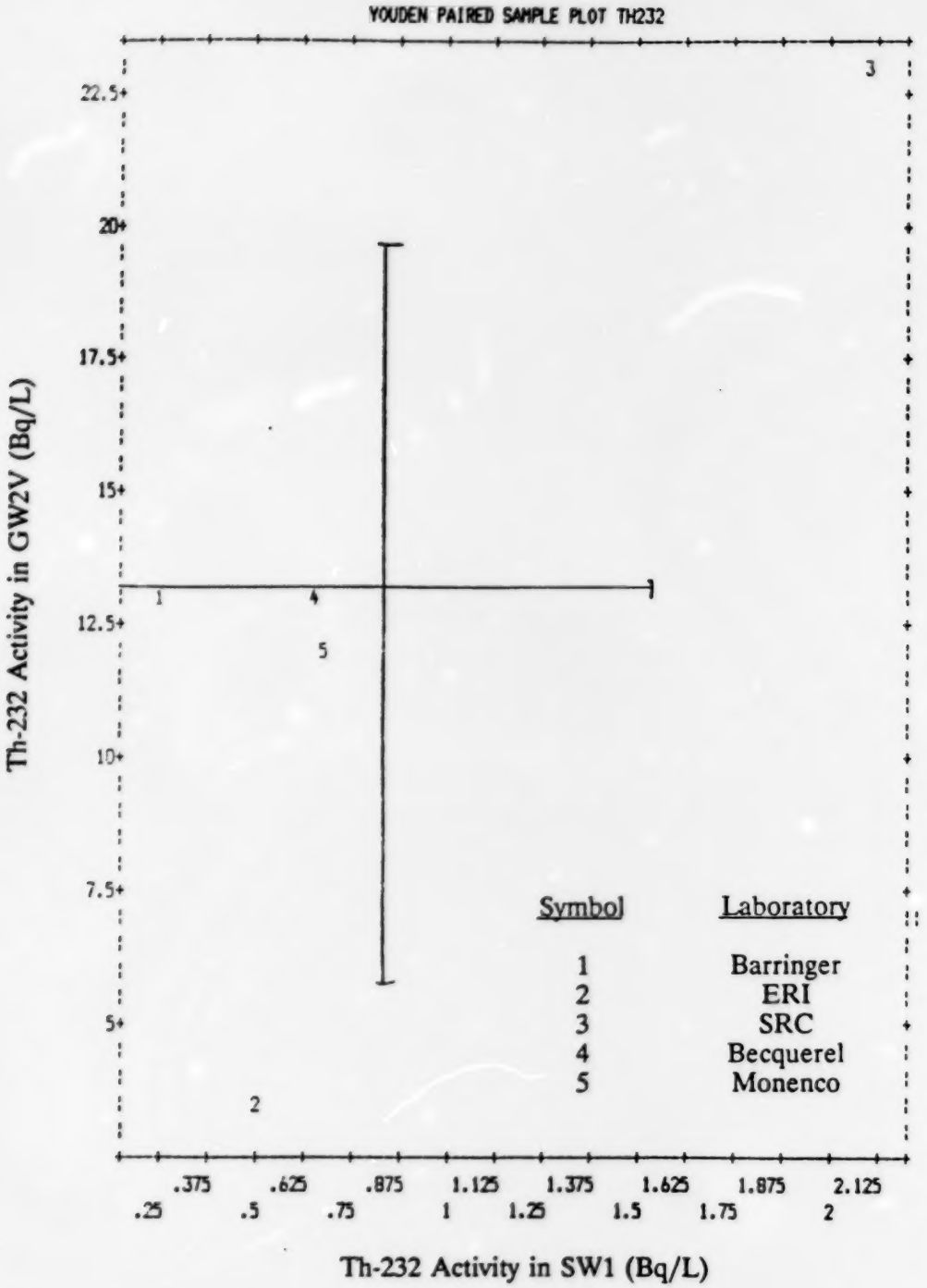
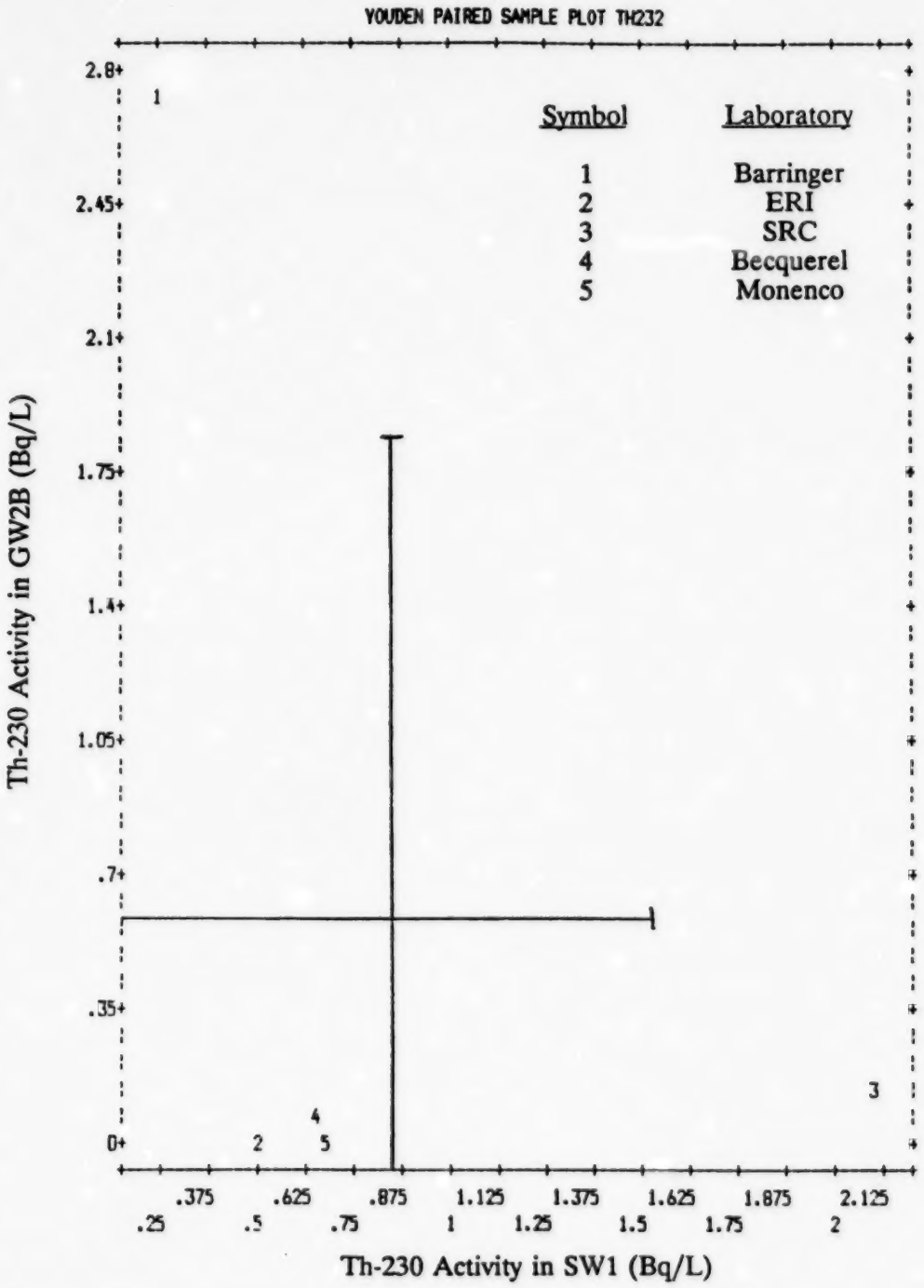


FIGURE 3.16: PAIRED SAMPLE PLOT OF TH-232 IN NATURAL SAMPLES GW2V AND SW1 (crossbars show interlaboratory SD)



5 cases plotted.
Use first digit of LABNO as plotting symbol and * for multiple occurrence.

FIGURE 3.17: PAIRED SAMPLE PLOT OF TH-230 IN SYNTHETIC SAMPLES GWLAB1 AND GWLAB2 (crossbars show interlaboratory SD)

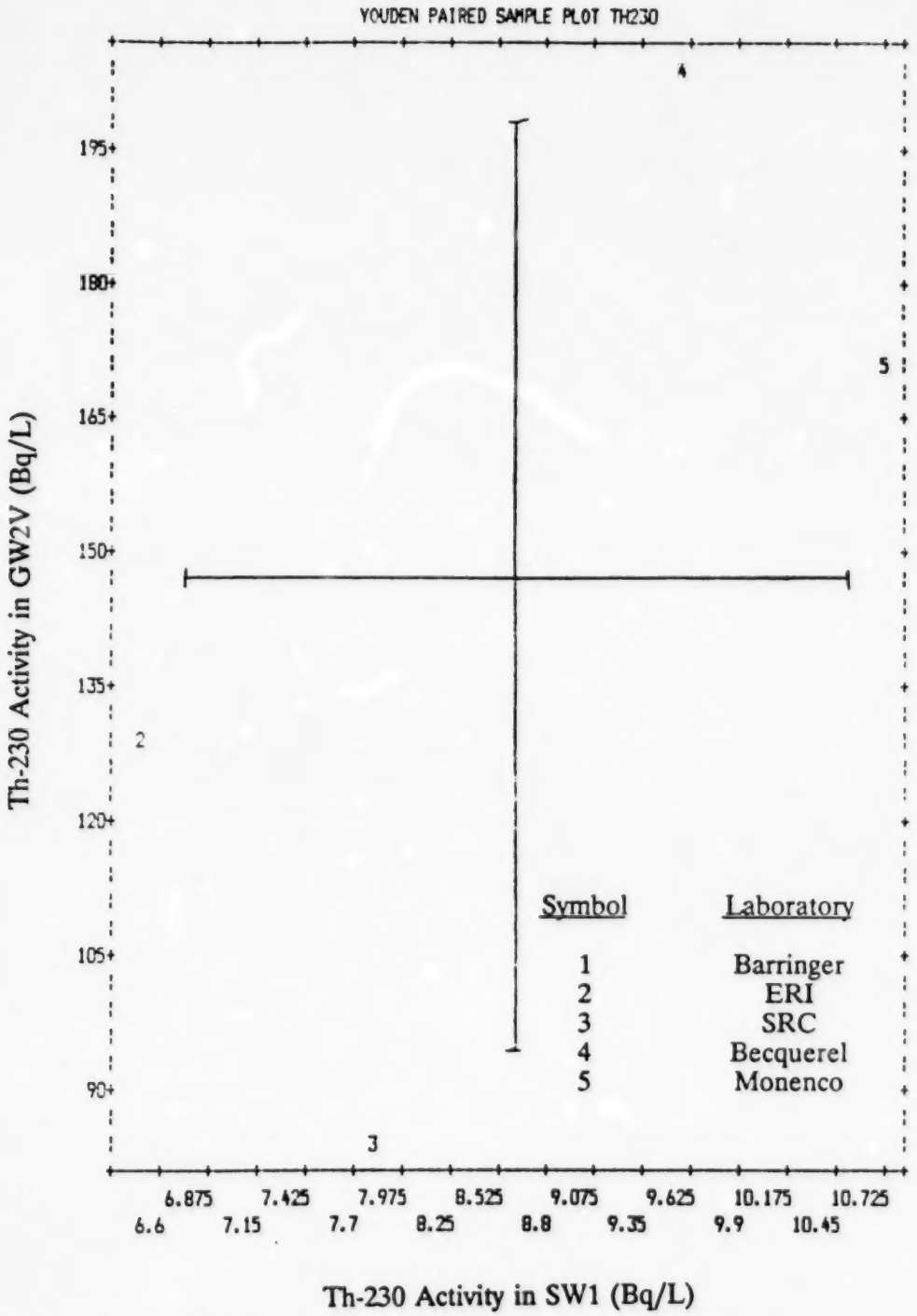


FIGURE 3.18: PAIRED SAMPLE PLOT OF TH-230 IN NATURAL SAMPLES GW2V AND SW1 (crossbars show interlaboratory SD)

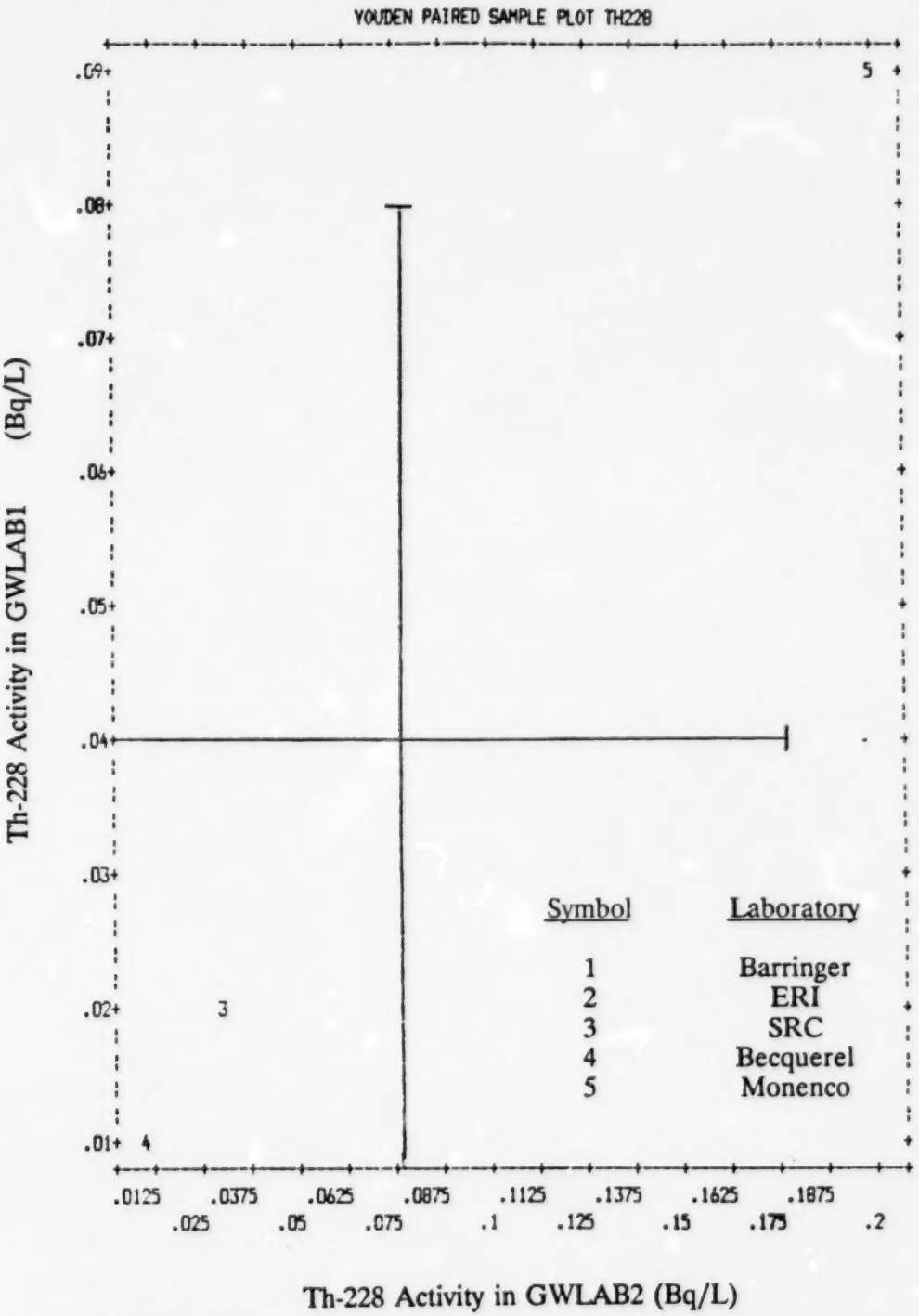


FIGURE 3.19: PAIRED SAMPLE PLOT OF TH-228 IN SYNTHETIC SAMPLES GWLAB1 AND GWLAB2 (crossbars show interlaboratory SD)

Figures 3.20 to 3.40: Figures Showing Youden-Paired Sample Plots for Examining Analytical Bias From Second Sample Submission (Figure 3.20 is Given in Main Body)

Plotting Symbol:	BAR = 1
Plotting Symbol:	ERI = 2
Plotting Symbol:	SRC = 3
Plotting Symbol:	BEQ = 4
Plotting Symbol:	MON = 5

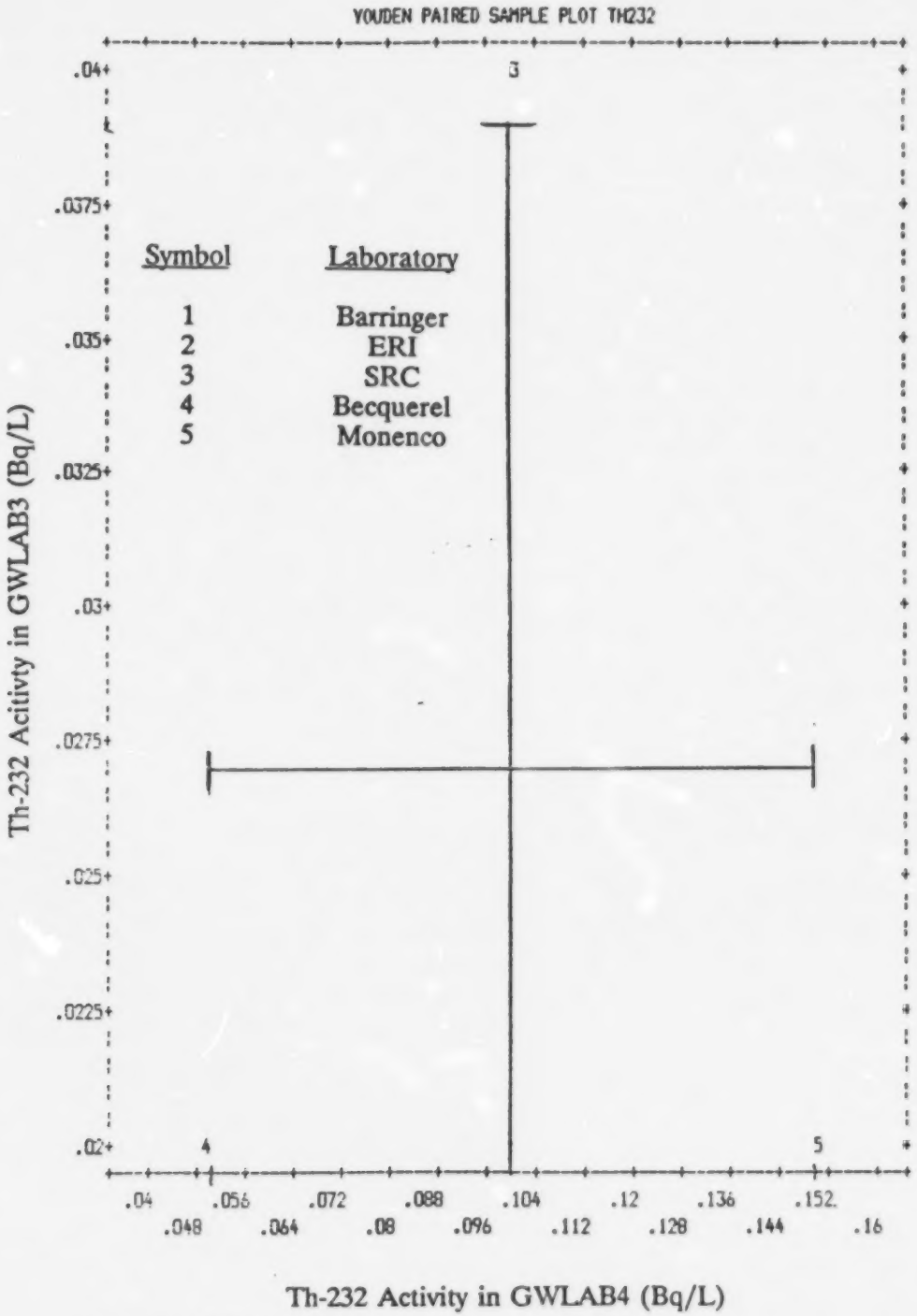


FIGURE 3.20: PAIRED SAMPLE PLOT OF TH-232 IN SYNTHETIC SAMPLES GWLAB3 AND GWLAB4 (crossbars show inter-laboratory SD)

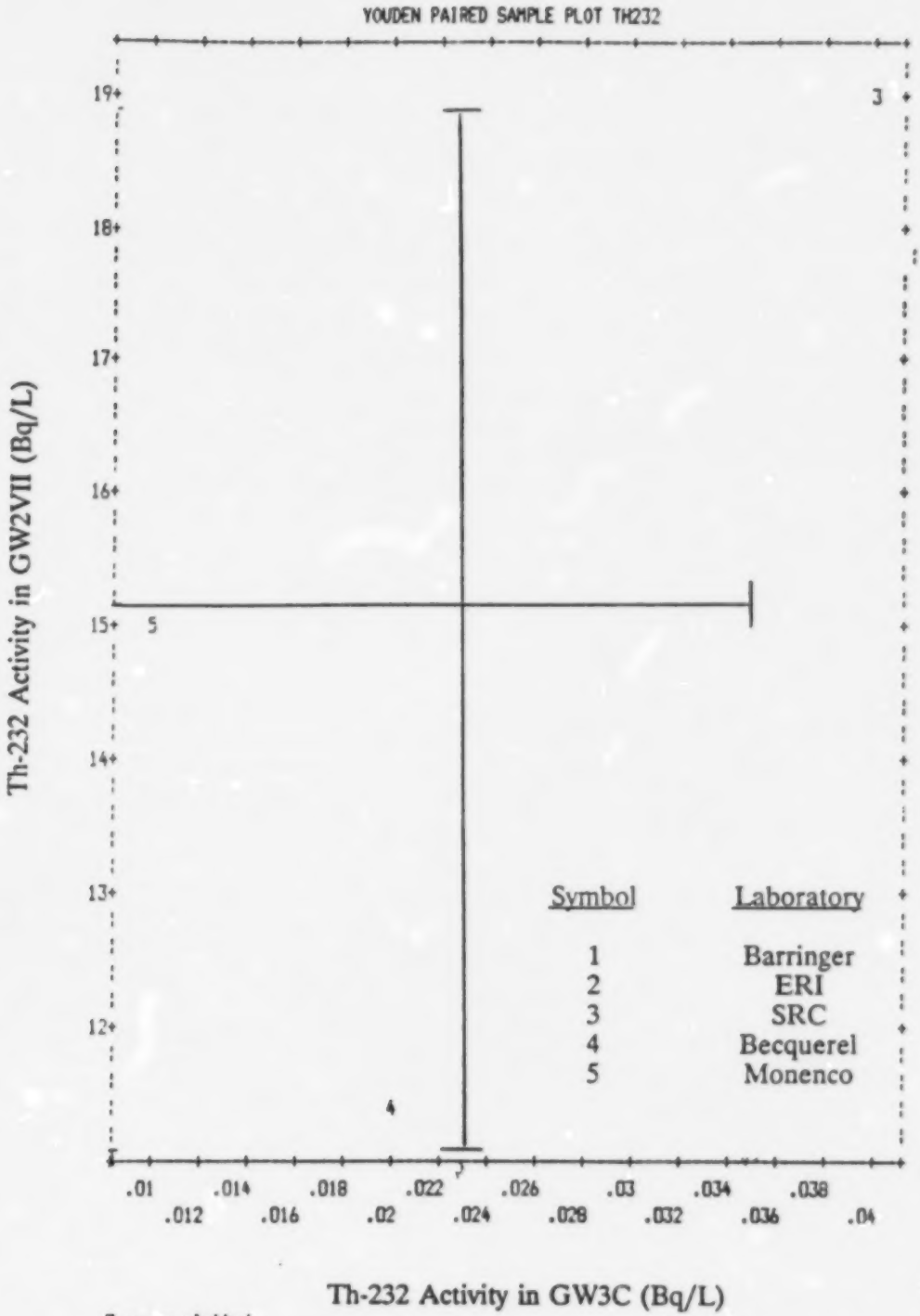


FIGURE 3.21: PAIRED SAMPLE PLOT OF TH-232 IN NATURAL SAMPLES GW2VII AND GW3C (crossbars show inter-laboratory SD)

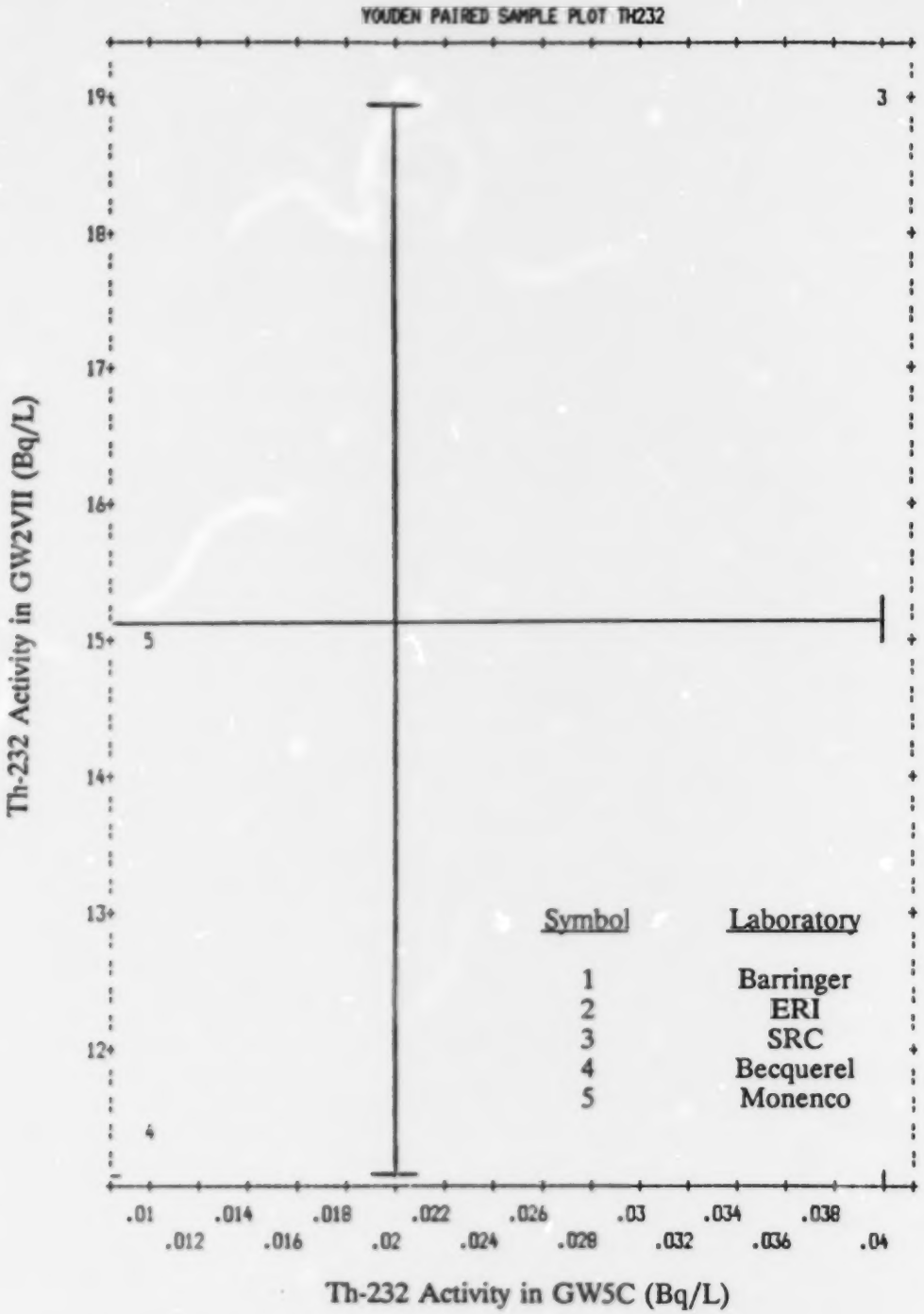
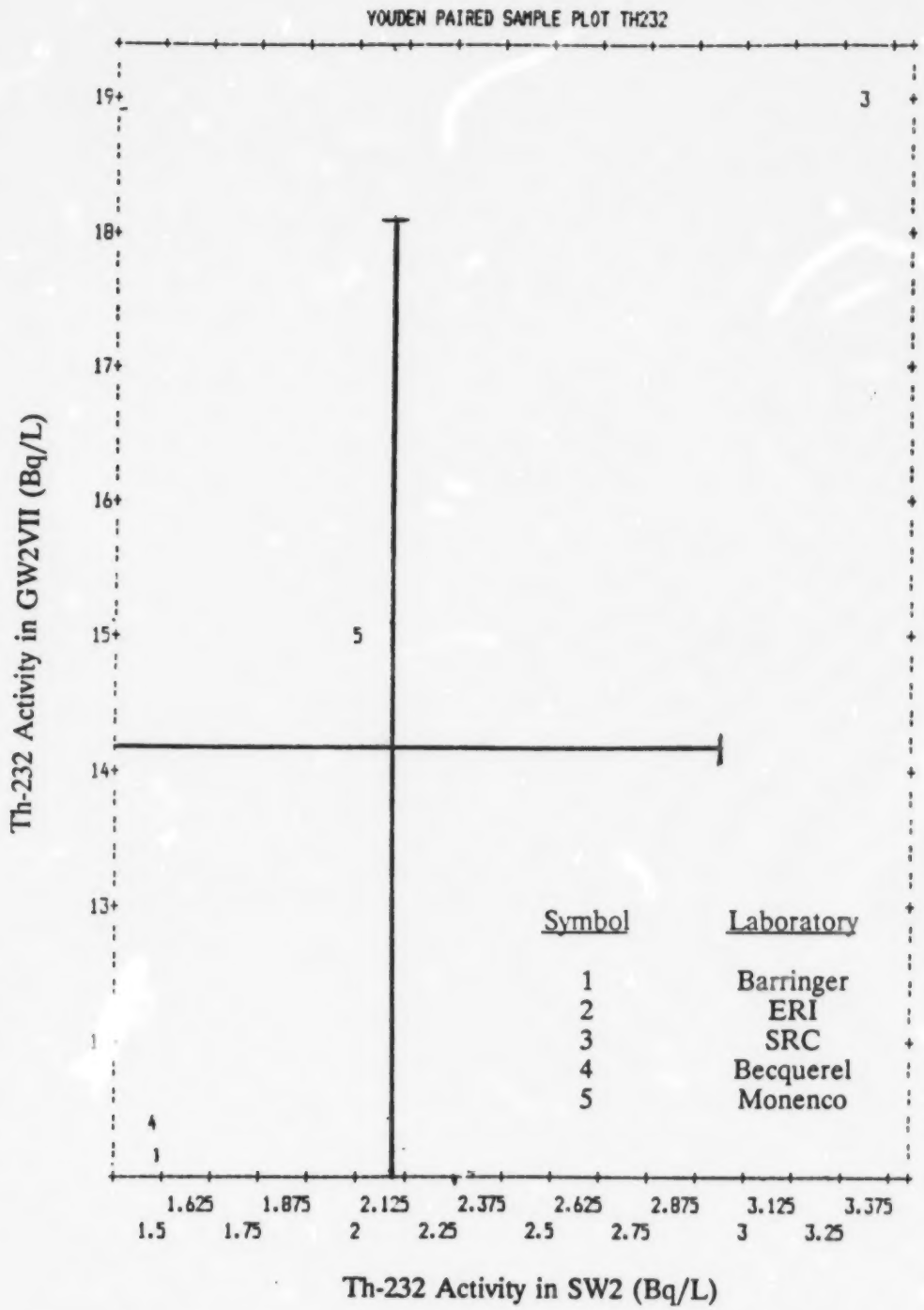


FIGURE 3.22: PAIRED SAMPLE PLOT OF TH-232 IN NATURAL SAMPLES GW2VII AND GW5C (crossbars show inter-laboratory SD)



3 cases plotted.
Use first digit of LABNO as plotting symbol and * for multiple occurrence.

FIGURE 3.23: PAIRED SAMPLE PLOT OF TH-232 IN NATURAL SAMPLES GW2VII AND SW2 (crossbars show inter-laboratory SD)

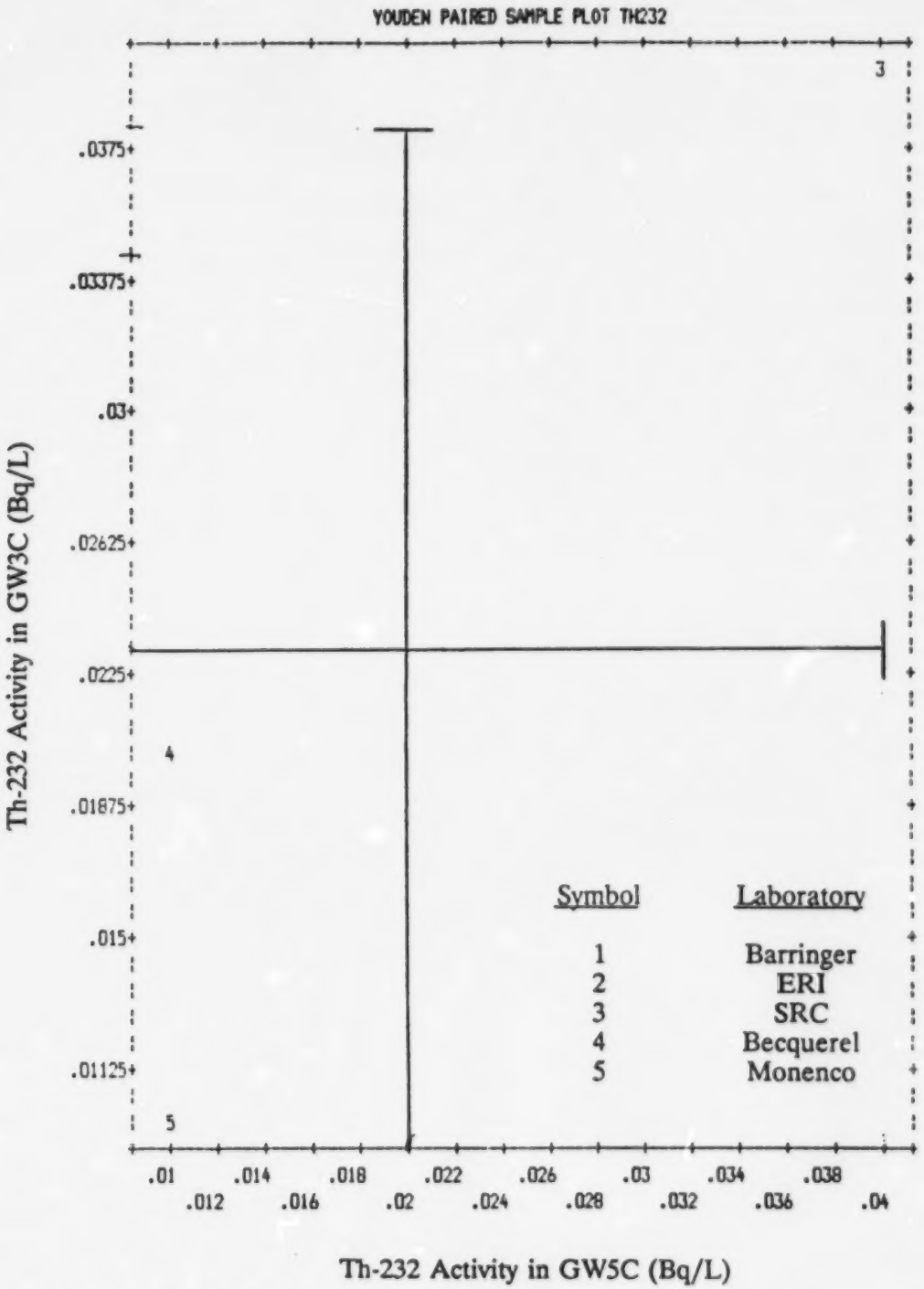


FIGURE 3.24: PAIRED SAMPLE PLOT OF TH-232 IN NATURAL SAMPLES GW3C AND GW5C (crossbars show inter-laboratory SD)

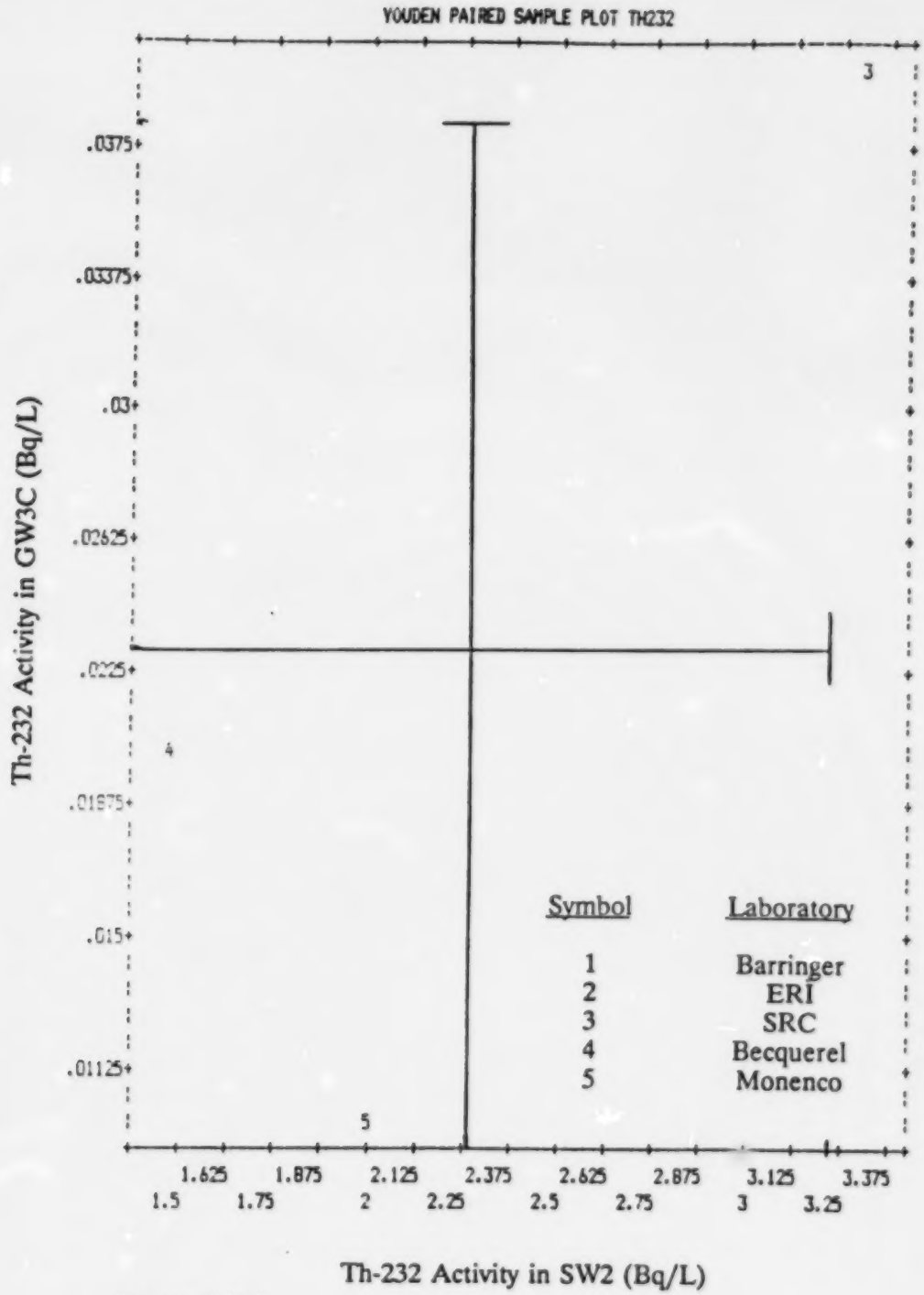


FIGURE 3.25: PAIRED SAMPLE PLOT OF TH-232 IN NATURAL SAMPLES GW3C AND SW2 (crossbars show inter-laboratory SD)

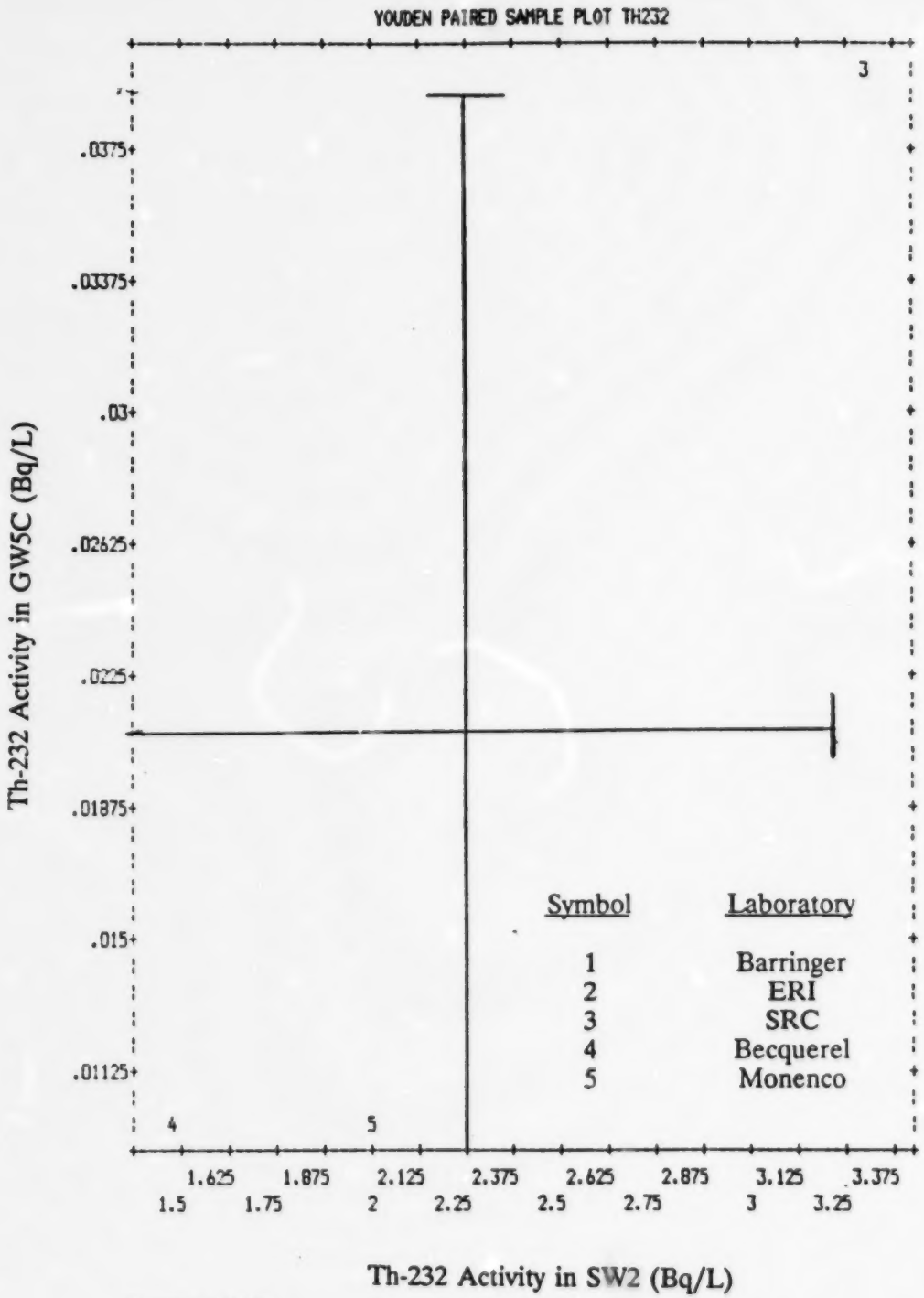


FIGURE 3.26: PAIRED SAMPLE PLOT OF TH-232 IN NATURAL SAMPLES GW5C AND SW2 (crossbars show inter-laboratory SD)

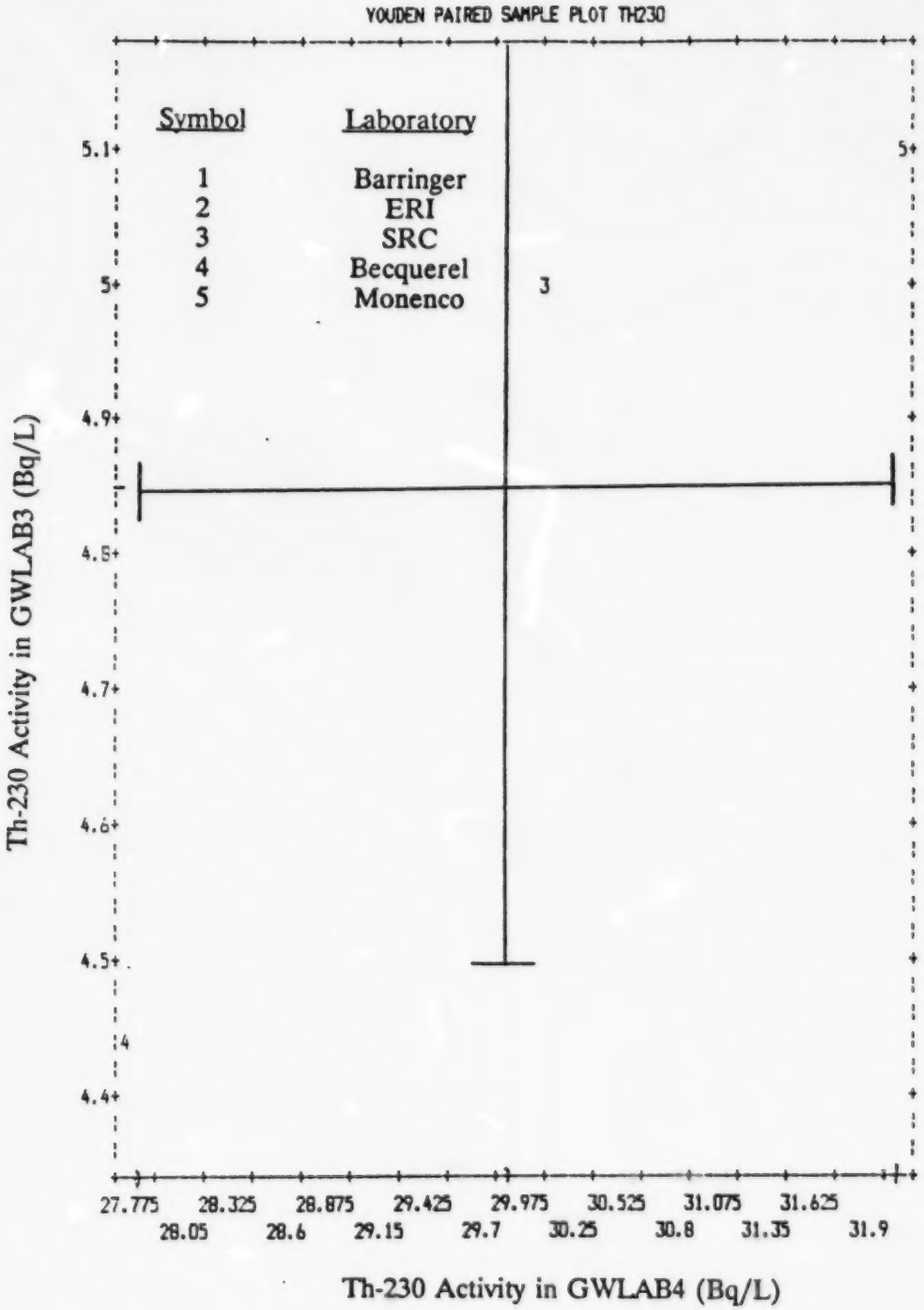


FIGURE 3.27: PAIRED SAMPLE PLOT OF TH-230 IN SYNTHETIC SAMPLES GWLAB3 AND GWLAB4 (crossbars show inter-laboratory SD)

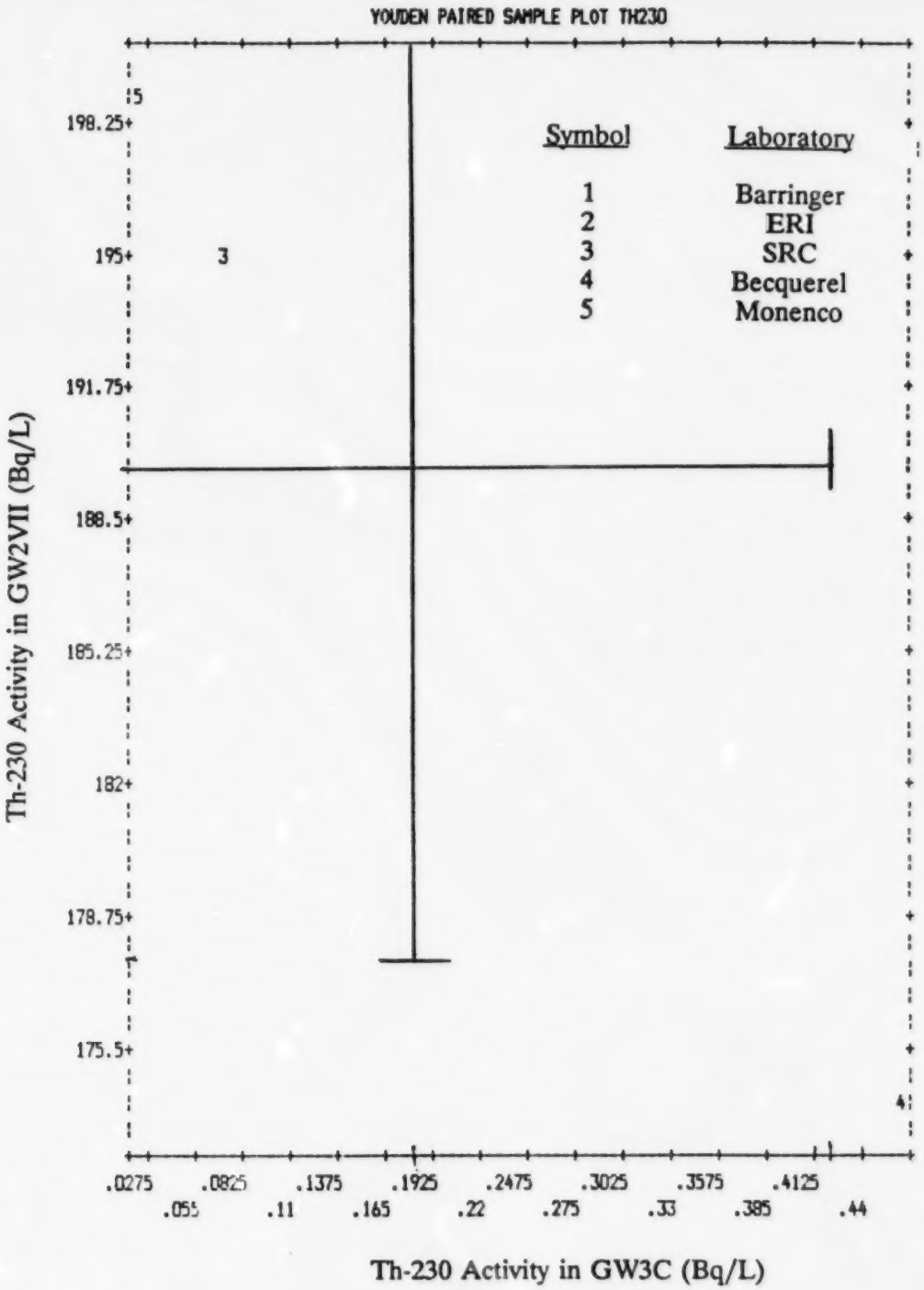


FIGURE 3.28: PAIRED SAMPLE PLOT OF TH-230 IN NATURAL SAMPLES GW2VII AND GW3C (crossbars show inter-laboratory SD)

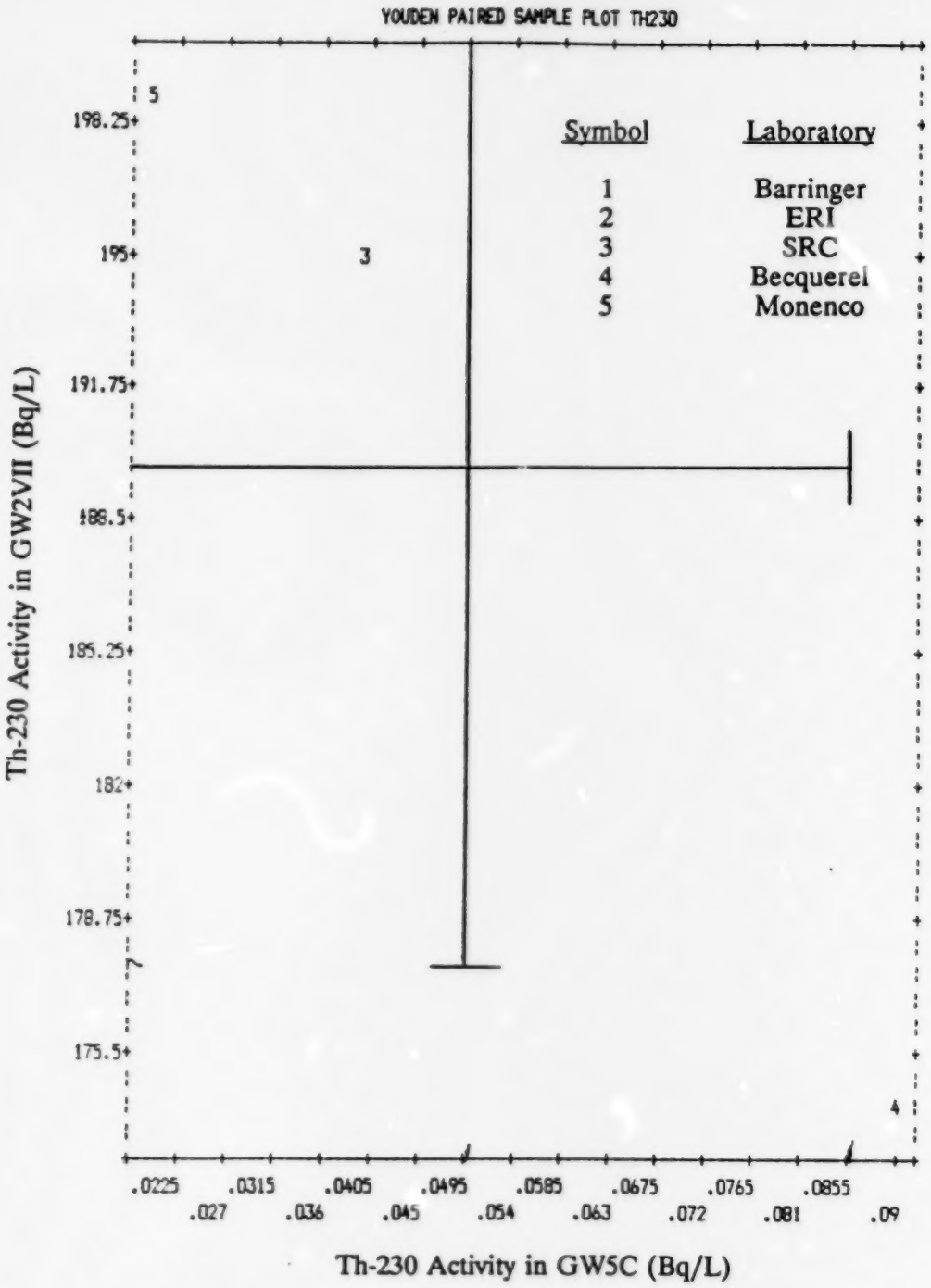


FIGURE 3.29: PAIRED SAMPLE PLOT OF TH-230 IN NATURAL SAMPLES GW2VII AND GW5C (crossbars show inter-laboratory SD)

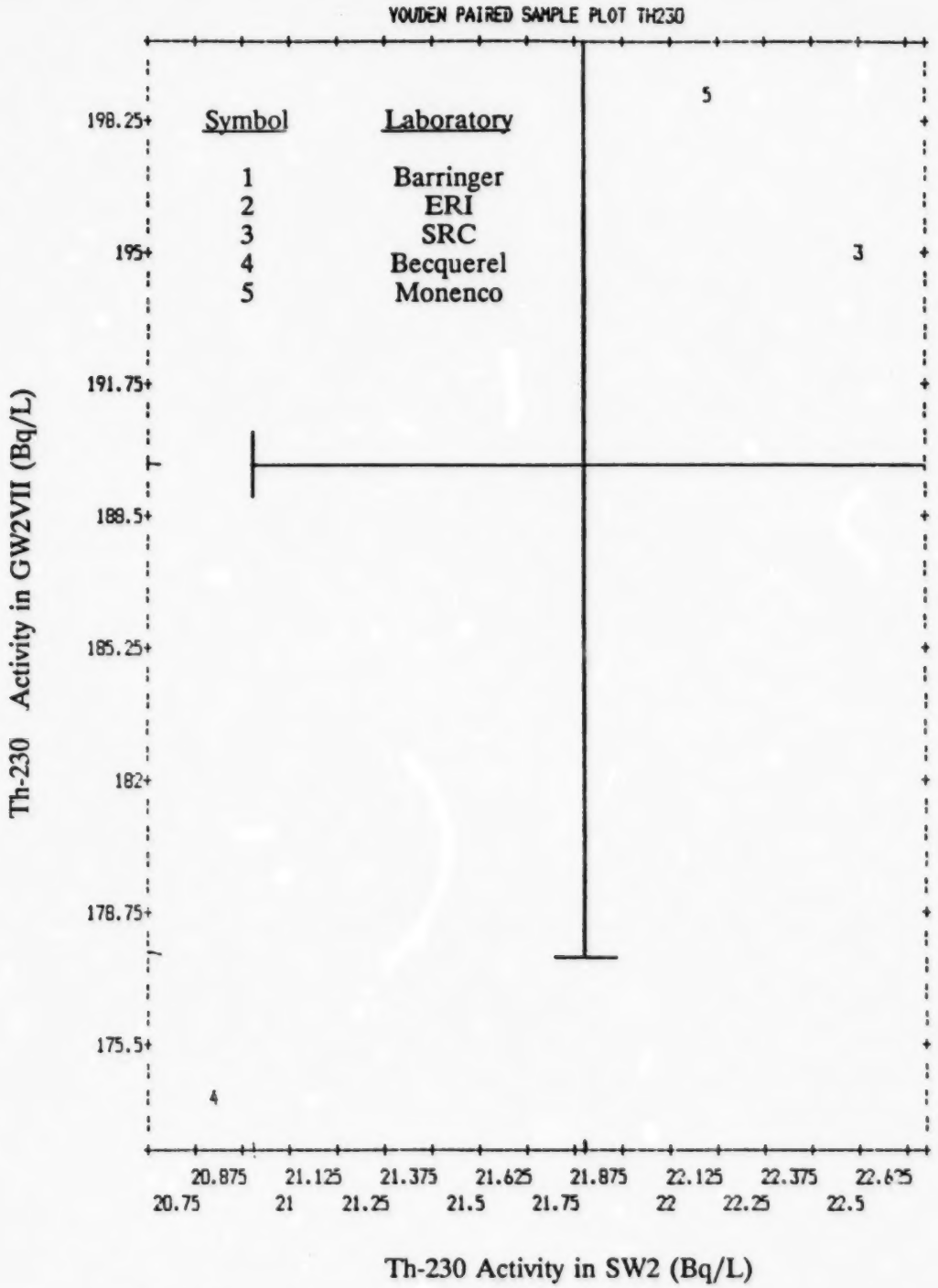


FIGURE 3.30: PAIRED SAMPLE PLOT OF TH-230 IN NATURAL SAMPLES GW2VII AND SW2 (crossbars show inter-laboratory SD)

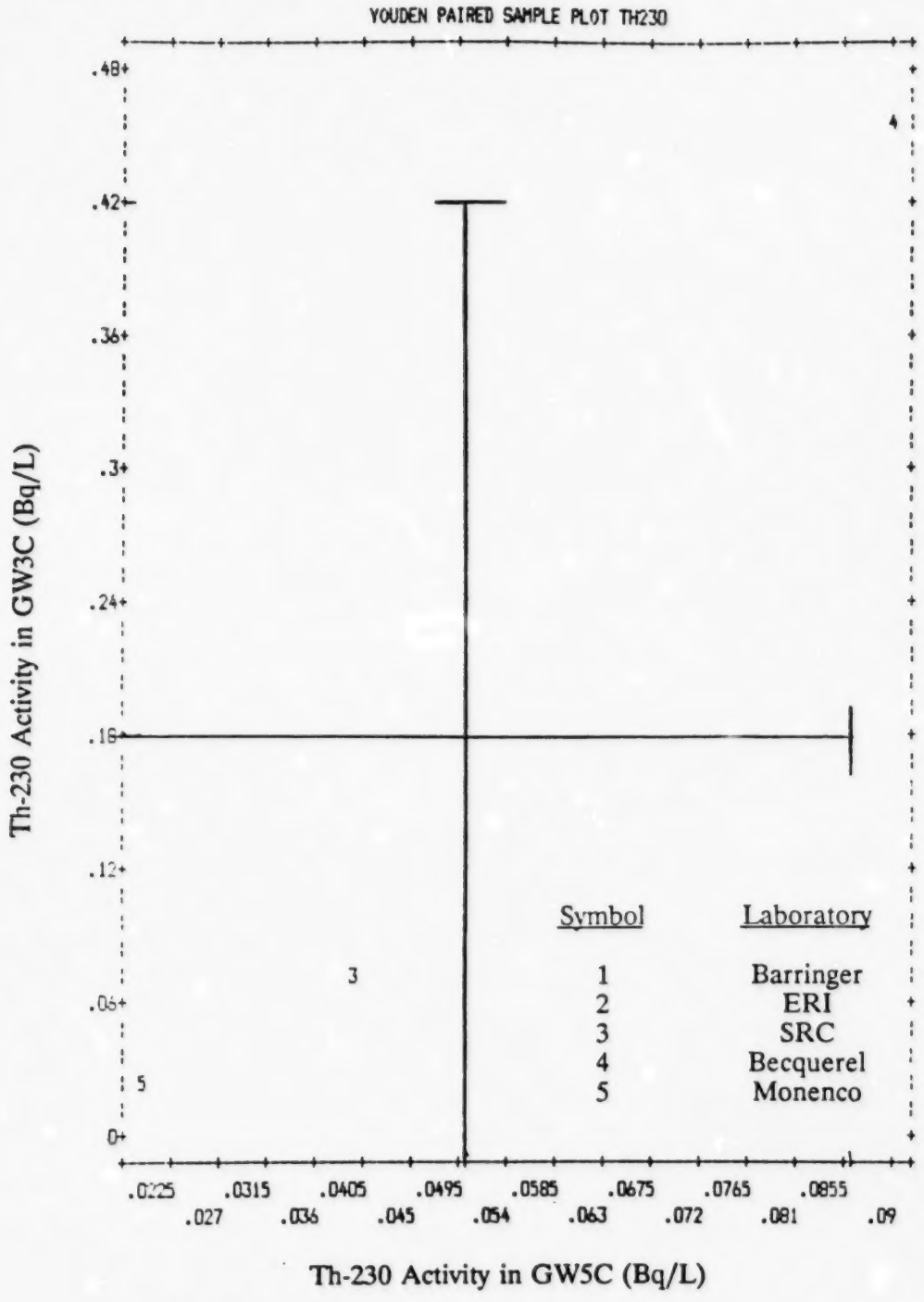


FIGURE 3.31: PAIRED SAMPLE PLOT OF TH-230 IN NATURAL SAMPLES GW3C AND GW5C (crossbars show inter-laboratory SD)

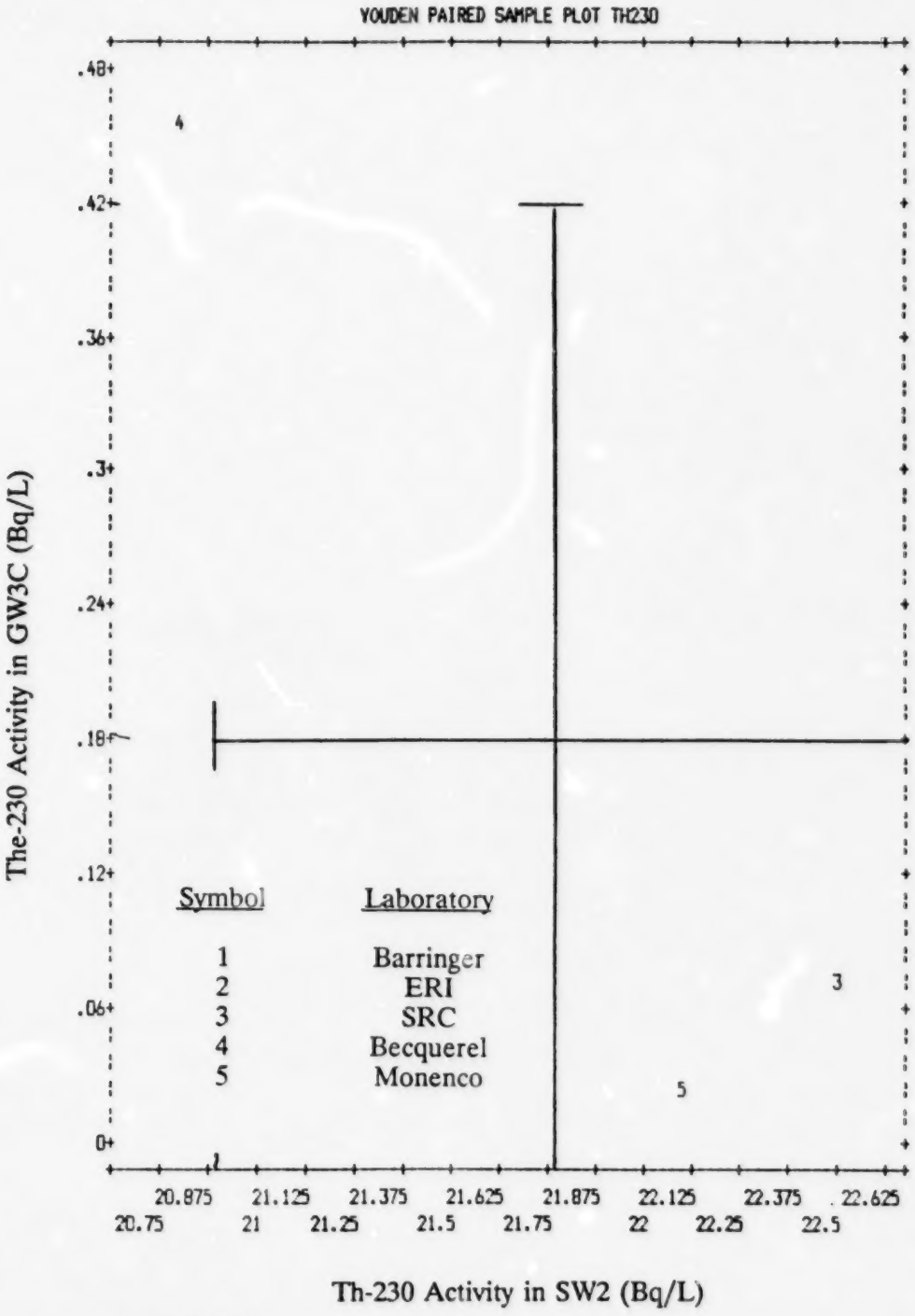


FIGURE 3.32: PAIRED SAMPLE PLOT OF TH-230 IN NATURAL SAMPLES GW3C AND SW2 (crossbars show inter-laboratory SD)

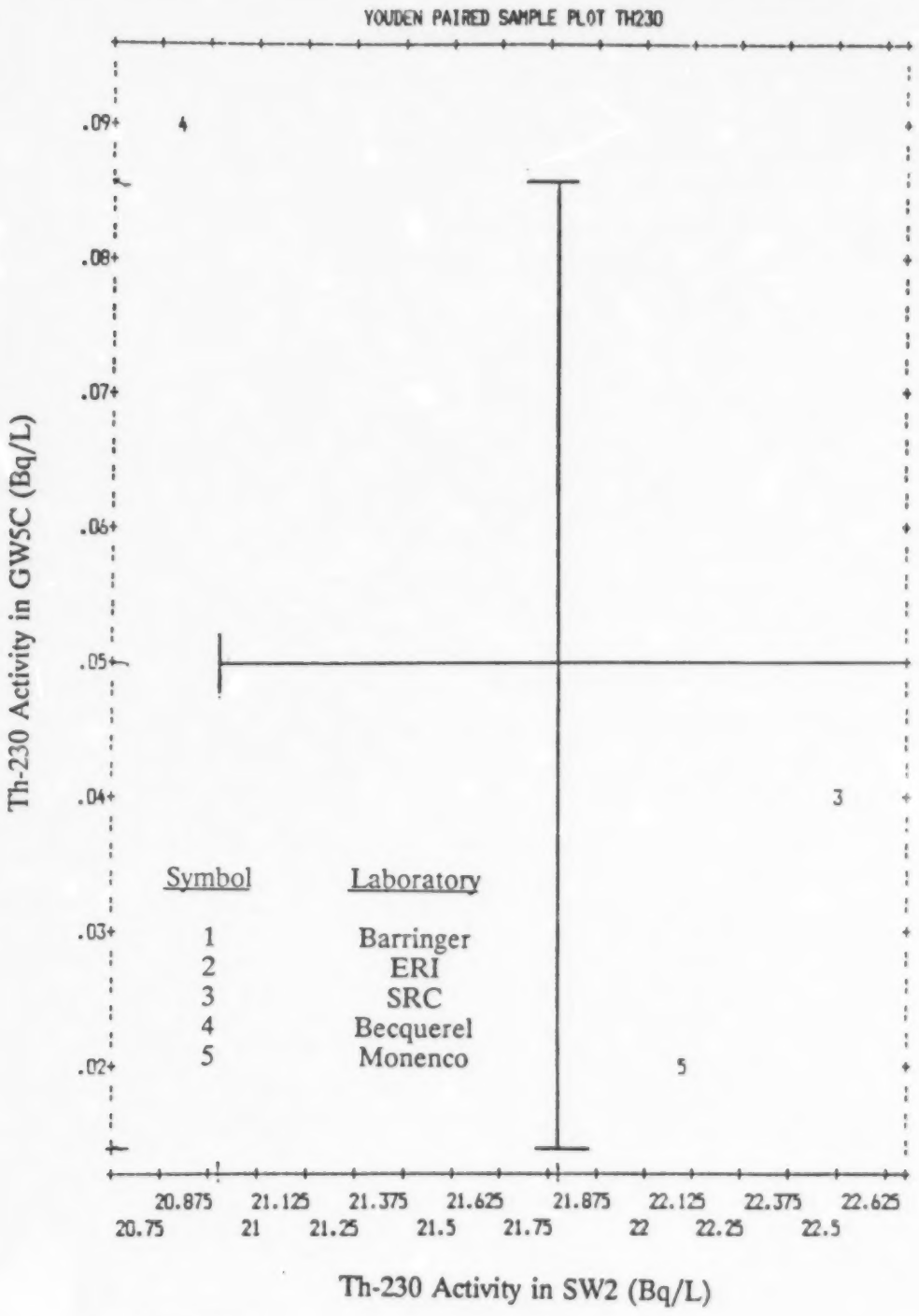


FIGURE 3.33: PAIRED SAMPLE PLOT OF TH-230 IN NATURAL SAMPLES GW5C AND SW2 (crossbars show inter-laboratory SD)

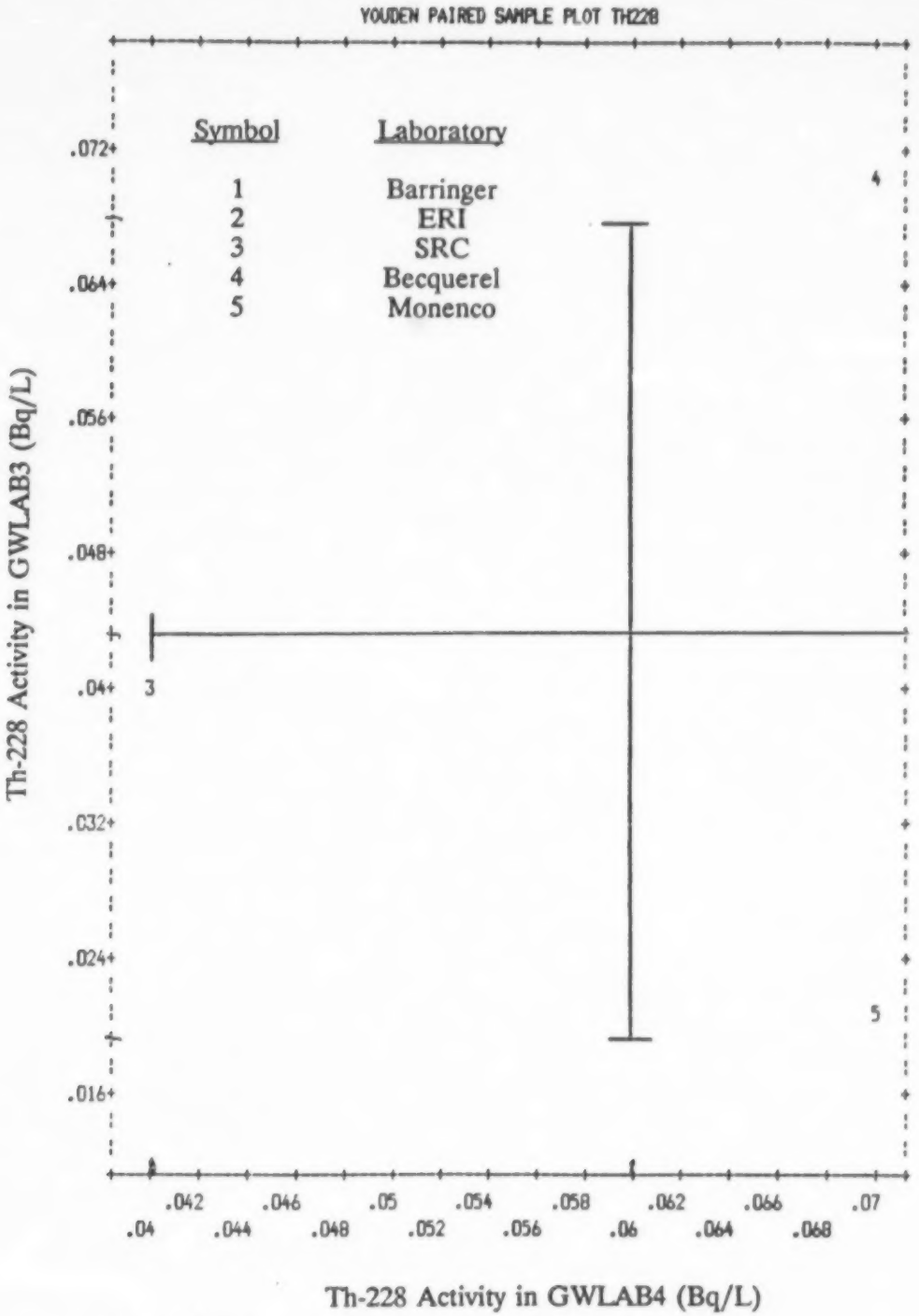


FIGURE 3.34: PAIRED SAMPLE PLOT OF TH-228 IN SYNTHETIC SAMPLES GWLAB3 AND GWLAB4 (crossbars show inter-laboratory SD)

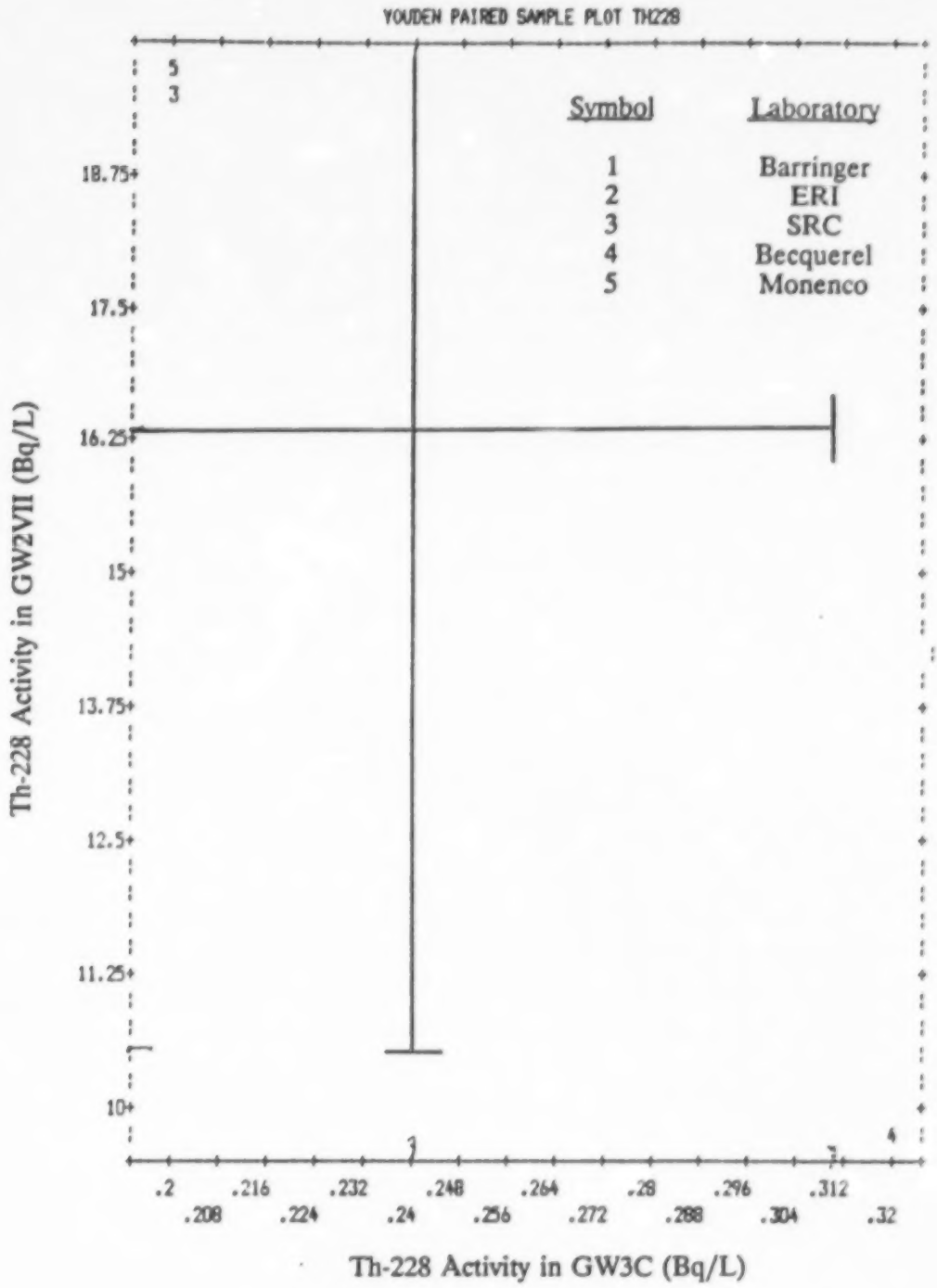


FIGURE 3.35: PAIRED SAMPLE PLOT OF TH-228 IN NATURAL SAMPLES GW2VII AND GW3C (crossbars show inter-laboratory SD)

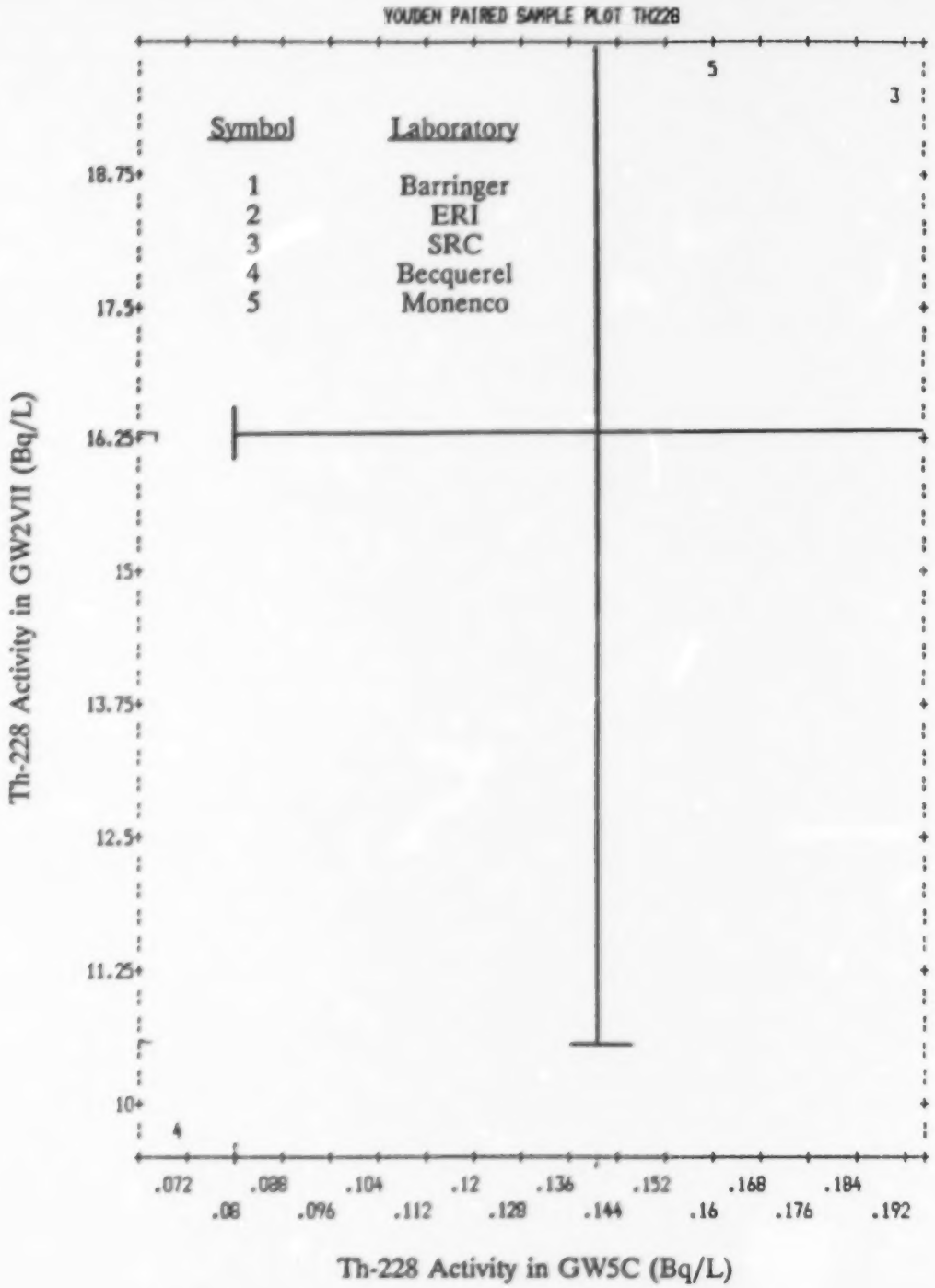


FIGURE 3.36: PAIRED SAMPLE PLOT OF TH-228 IN NATURAL SAMPLES GW2VII AND GW5C (crossbars show inter-laboratory SD)

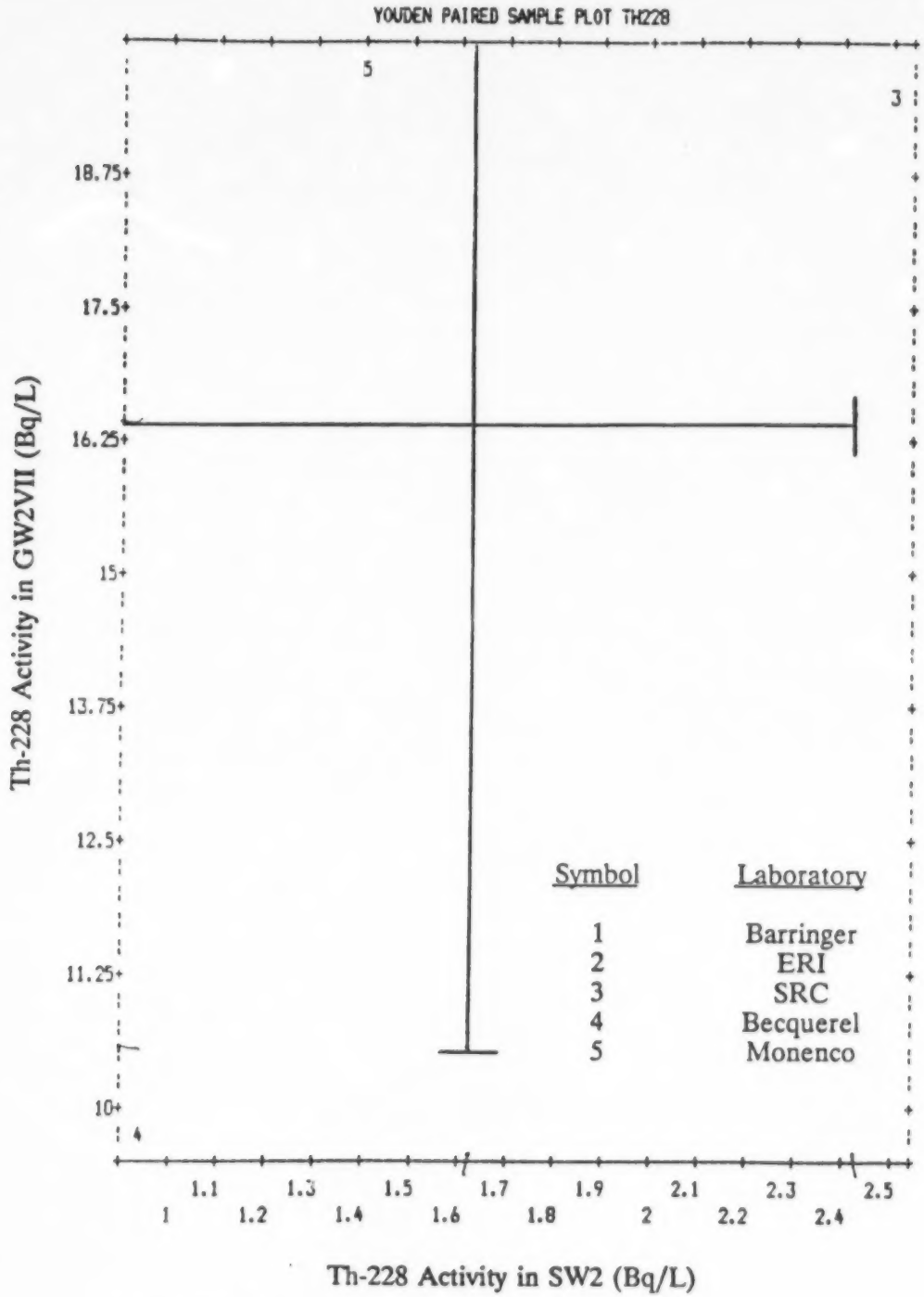
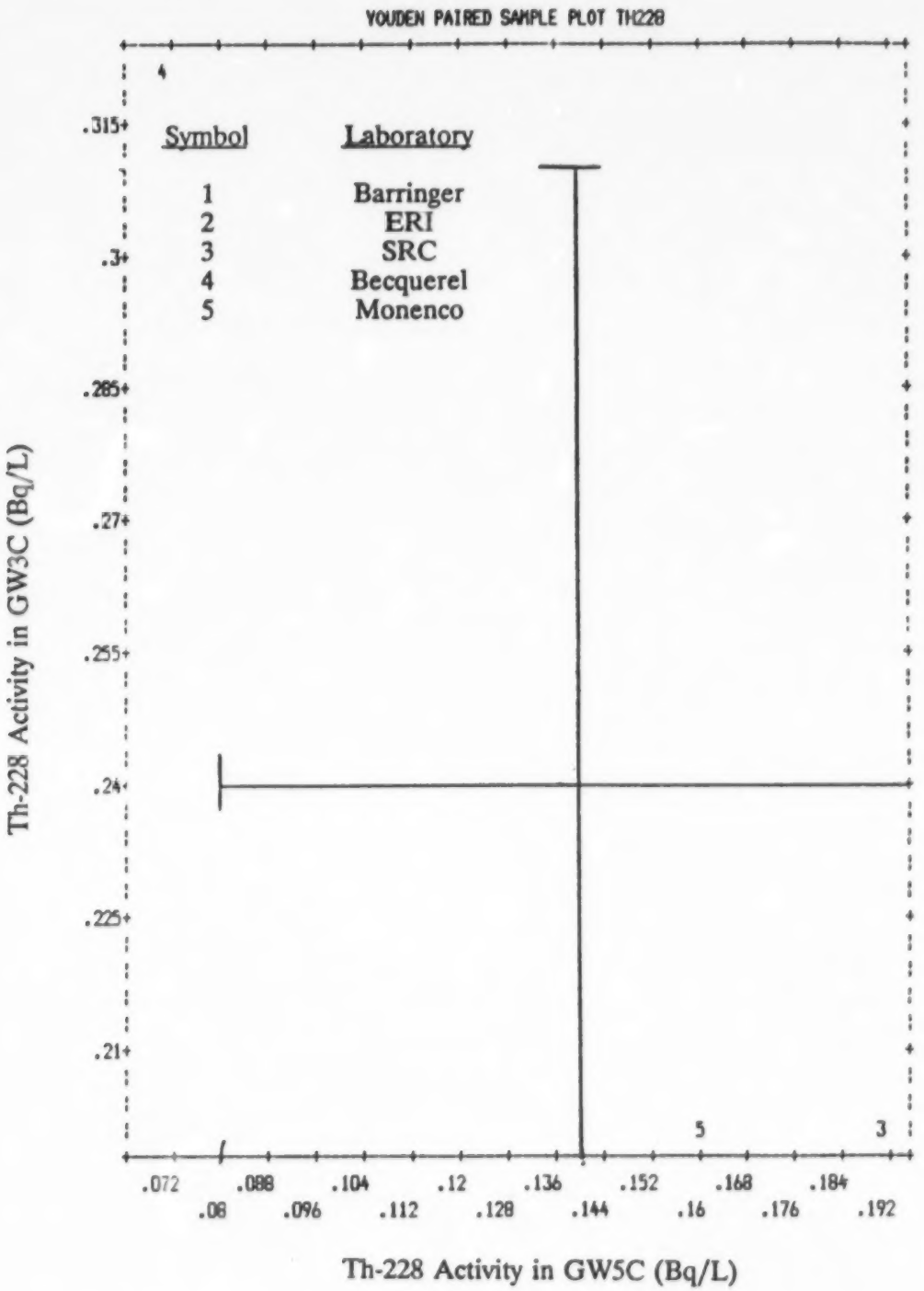


FIGURE 3.37: PAIRED SAMPLE PLOT OF TH-228 IN NATURAL SAMPLES GW2VII AND SW2 (crossbars show inter-laboratory SD)



3 cases plotted.
Use first digit of LABNO as plotting symbol and $ for multiple occurrence.

FIGURE 3.38: PAIRED SAMPLE PLOT OF TH-228 IN NATURAL SAMPLES GW3C AND GW5C (crossbars show inter-laboratory SD)

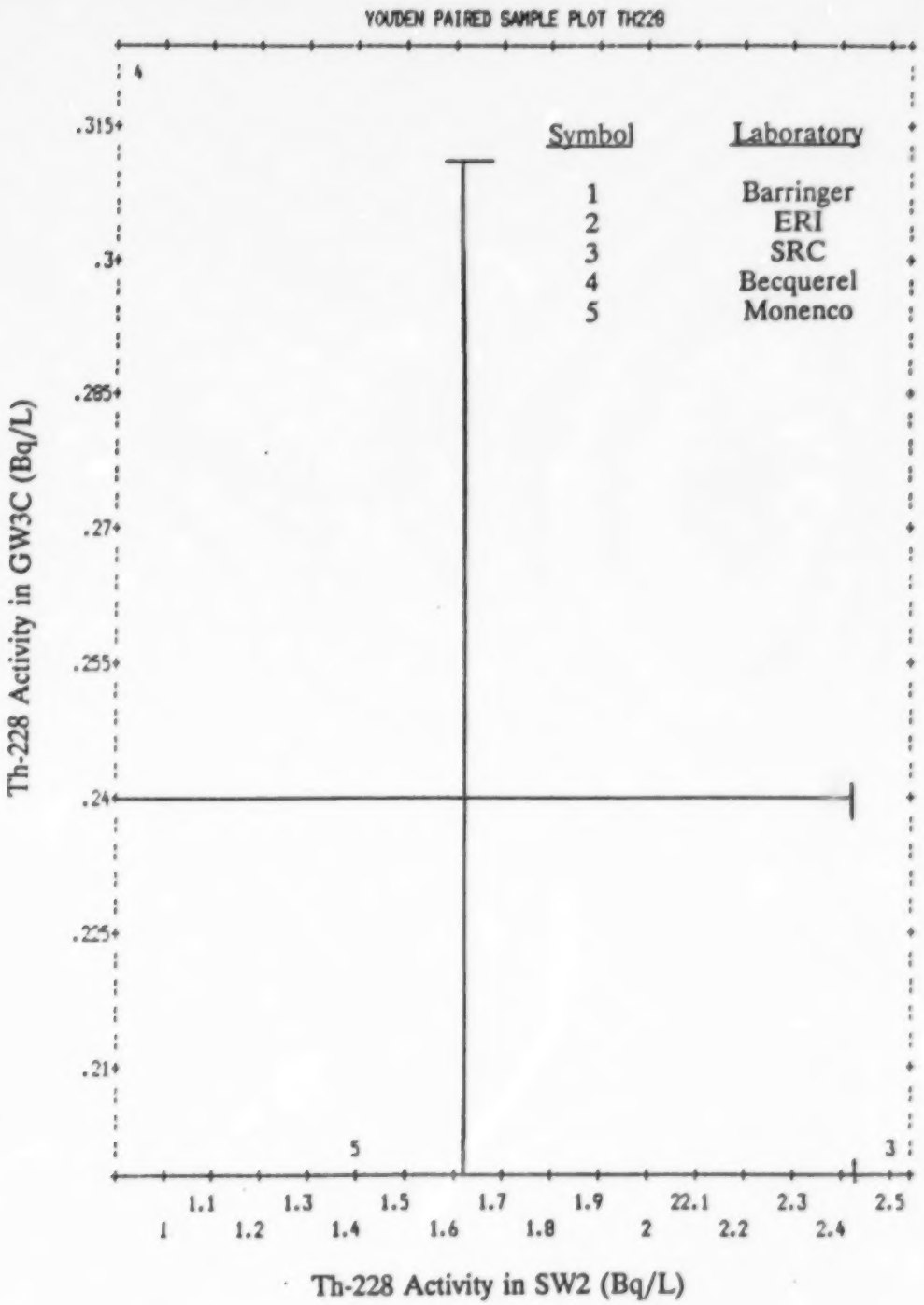


FIGURE 3.39: PAIRED SAMPLE PLOT OF TH-228 IN NATURAL SAMPLES GW3C AND SW2 (crossbars show inter-laboratory SD)

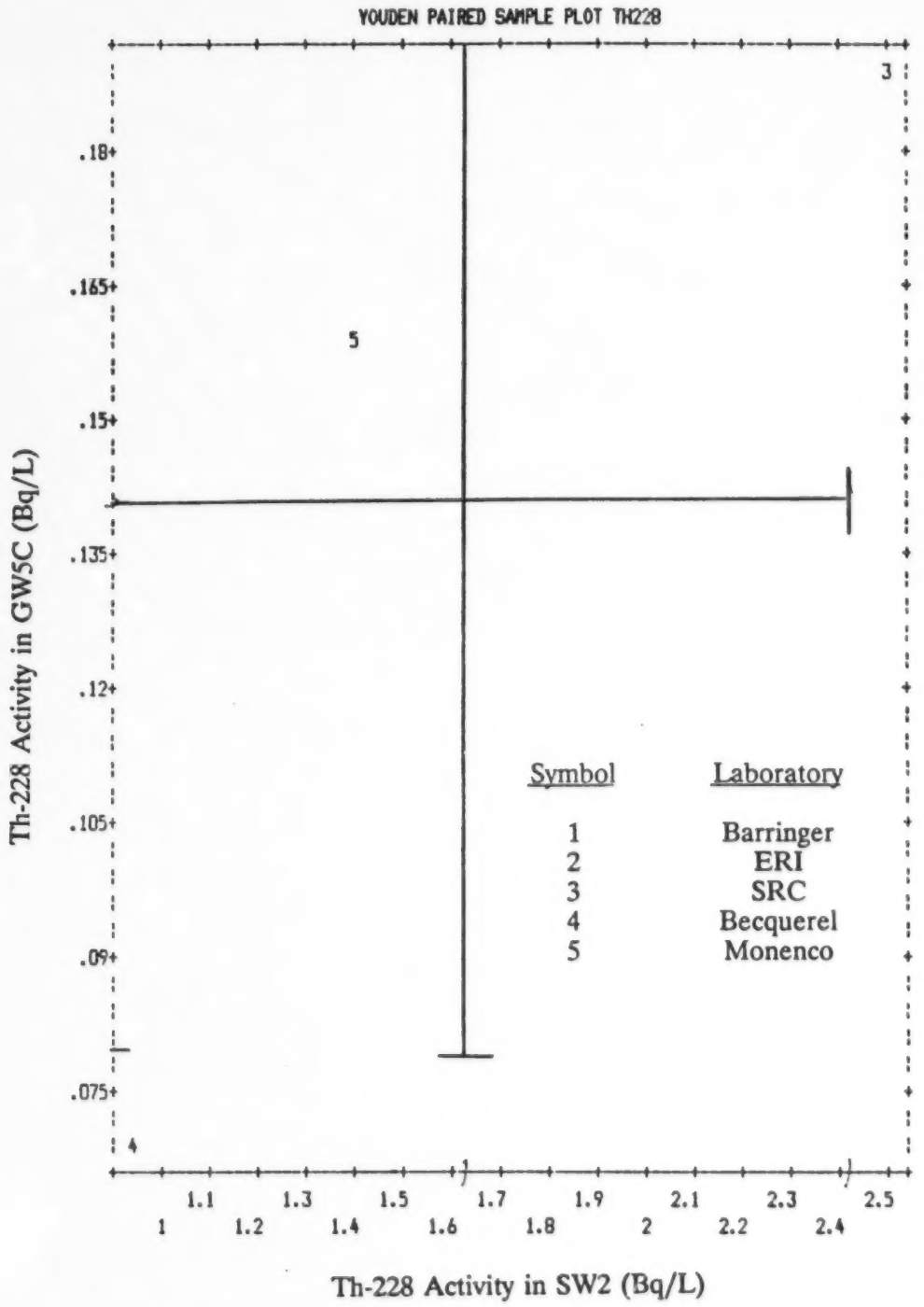


FIGURE 3.40: PAIRED SAMPLE PLOT OF TH-228 IN NATURAL SAMPLES GW5C AND SW2 (crossbars show inter-laboratory SD)